Andrew E. Moore

Issued with August Number, 1895.

Proceedings.

COUNCIL.

A committee consisting of Professors Hale, Austen and Breneman, has been appointed by the President to consider the question of a permanent badge for the Society.

NEW MEMBERS ELECTED JUNE 6.

Beal, Prof. James H., Scio College, Scio, Ohio.
Chauvenet, Wm. M., 709 Pine St., St. Louis, Mo.
Fuller, Geo. W., Experiment Station, Lawrence, Mass.
Gaylord, Wallace R., 146 Terrace Drive, Passadena, Cal.
Harrison, John B., Government Laboratory, Georgetown, Demerara, British Guiana.
Hengstler, Louis, Jr., Hoboken, N. J.
Howard, Chas. D., S.B., Newport, R. I.
Lagai, P. G., Ph.D., 17 Park Place, New York City.
Linebarger, C. E., South Division, High School, Chicago, Ill.
McBryde, J. Bolton, University of Tenn., Knoxville, Tenn.
McClure, Prof. Edgar, University of Oregon, Eugene, Ore.
Pagelson, Otto H., 2421 Dearborn St., Chicago, Ill.
Peacock, Samuel, 47 South 17th St., Philadelphia, Pa.
Rich, H. L., Lasell Seminary, Auburndale, Mass.
Richardson, Geo. M., Stanford University Cal.
Wellington, Harry T., Wellington Manufacturing Co., 468 and 470 Cherry St., New York City.

CHANGES OF ADDRESS.

Barba, W. P., 5110 Newhall St., Germantown, Phila., Pa.
Brown, Lucius P., 150 North Cherry St., Nashville, Tenn.
Behr, Arno, 171 Grand Ave., Passadena, Cal.
Benton, Geo. W., High School, Indianapolis, Ind.
Bird, Herbert S., care of N. Y. Tartar, Co., 9th St. and Gowanus Canal, Brooklyn, N. Y.
Cambier, Jacob, 1000 Abriendo Ave., Pueblo, Colo.
Carpenter, Thos. B., 325 Jersey St., Buffalo, N. Y.
Chase, Geo. W., Thomas, Ala.
Clapp, Geo. H., 325 Water St., Pittsburg, Pa.
Collins, W. H., 6757 Perry Ave., Chicago, Ill.
Clymer, Edwin S., 45-47 Reed St., Reading, Pa.

Doolittle, O. S., 130 North 5th St., Reading, Pa.
Evans, Thomas, Chemist American Cotton Oil Co., 46 Cedar St., New York City.
Feid, George F., 199 Findlay St., Cincinnati, Ohio.
Hochstetter, Robert W., Oak and Bellevue Sts., Mt. Auburn, Cincinnati, Ohio.
Linn, A. F., Park Place, Springfield, Ohio.
Lustig, A. L., P. O. Box 582, Providence, R. I.
Maxwell, Dr. Walter, Sugar Experiment Station, Honolulu, S. I.
Nichols, Wm. H., 47 Cedar St., New York City.
Pearce, Edward D., care of L. P. Shepard and Co., Providence, R. I.
Powell, J. W. Bureau of Ethnology, Washington, D. C.
Rosengarten, Geo. D., 1700 Fitzwater St., Philadelphia, Pa.
Schimpf, Henry W., 365 Franklin Ave., Brooklyn, N. Y.
Simonson, W., 901 Race St., Cincinnati, Ohio.
Smith, Thorn, Agricultural College, Lansing, Mich.
Stone, W. G., 302 Union St., Brooklyn, N. Y.
Taylor, Thomas, M.D., 238 Massachusetts Ave., N. E., Washington, D. C.
Waller, Elwyn, 440 First Ave., New York City.
Wesson, David, University Heights, N. Y.
Wickhorst, Max H., 268 Forquer St., Chicago, Ill.
Wood, E. F., Munhall, Pa.
Wood, Edward S., 688 Boylston St., Boston, Mass.
Wulf, Henry C., care of Pacific Mill Co., San Francisco, Cal.
Youmans, W. J., 72 Fifth Ave., New York City.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The March meeting was held Thursday evening, March 21. J. P. Famworth, Esq., read a paper on the "Selection of Water for Bleaching and Other Manufacturing Purposes."

The April meeting was held Thursday evening, April 23. Mr. H. S. Bingen presented a paper entitled "A Resumé of the Methods of Bleaching Cotton Piece Goods."

The May meeting was held Thursday, May 23. Edward D. Pearce, Esq., presented a paper on "Pollen." The paper contained suggestions as to the nature of the color of pollen grains, with a review of methods of mounting, and the effect upon the coloring-matter of various mounting media. The paper was

illustrated by twenty-five typical slides exhibited under the microscope.

The June meeting was held Thursday, June 13th, 12 m. This being also the Annual meeting, the first business was the election of officers for the ensuing year, which resulted as follows: Presiding Officer, Mr. Charles A. Catlin; Secretary and Treasurer, Prof. Walter M. Saunders; Member of the Executive Committee, Mr. George F. Andrews.

After the transaction of other business relating to the work of the Section for the coming year, the Chairman presented his annual address, taking as his topic, "Chemical Laboratory Microscopy," advocating a more thorough training of young chemists in microscopy, specially and directly applied to chemical laboratory work. Presenting and discussing recent advances in micro-physiography, crypto-chemistry, and micro-chemical reactions, he described and illustrated some original methods and apparatus of his own, more particularly a method of mounting for the purpose of localizing the individual particles in samples of powdered material, by means of adhesive films upon slides having engraved or etched numbered squares, thus fixing each in certain definite portions for purpose of subsequent identification through optical behavior, physical form, or reaction with reagents. He further suggested and illustrated the valuable service that may be obtained from cultures of some of the lower organisms in the classification of turbid solutions, more especially, the removal of suspended finely divided carbon, such as at times results from the carbonizing of organic matter in the presence of fluxing and other salts, the suspended matter of such solutions being attracted and entangled in the mycelium of the fungus growth induced therein, and thus with it easily removed. He finally discussed micro-chemical reactions in their bearing upon qualitative chemical analysis, urging a more complete classification of the facts relating to reactions already studied, with the view of elaborating a less complicated scheme of micro-chemical analysis than any suggested, commending the works of Klément and Rénard, of Haushofer and of Behrens, as worthy of confidence. In his own work he found the greatest usefulness of micro-chemical analysis, not in any scheme, but as auxiliary

to the ordinary course of qualitative analysis, through special reactions curtailing oftimes to a remarkable degree its tedious separations, and further, finding in it an approximate qualitative value far exceeding the indications of ordinary qualitative work in this direction; and suggested possibly the attainment of very close approximations quickly, by comparison of reactions with standards of known value.

During an intermission, the members in attendance enjoyed a delightful lunch in one of the private dining rooms of the famous Hope Club.

CINCINNATI SECTION.

The meeting was held Wednesday, May 15, Dr. Alfred Springer presiding.

Mr. Henry B. Foote read a paper on "The Adulteration of Powdered Elm Bark." He stated that in his opinion the microscope was the only reliable means of detecting adulterations in the powdered bark. He thought no reliance should be placed on the starch test, as the liber of young trees contained starch but no reaction could be obtained from bark from old trees.

Prof. T. H. Norton read a paper on "Ammonium Thioacetate." After speaking of the many advantages of this over hydrogen sulphide as a precipitant, he demonstrated practically the ease with which the arsenites and arsenates could be completely precipitated from solution.

Adjourned until October 15.

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THE CHEMICAL NATURE OF DIASTASE.[1]

BY THOMAS B. OSBORNE.

Received April 2, 1895.

FEW substances are of more importance or of more interest than the enzymes or unorganized ferments, yet our knowledge relating to these bodies is almost wholly confined to the products of their activity and the conditions under which this is manifested. Although the existence of these ferments was recognized early in the present century, our information in respect to their true nature is exceedingly limited and unsatisfactory. It was for a long time supposed that the active substance causing a fermentative change is a soluble proteid, and the power of inducing such change seems by many to have been ascribed to soluble proteid matter in general. Later, this power was thought to be restricted to special forms of proteid, but no sufficient evidence was brought forward. Of late years investigators have undertaken to isolate ferments and prepare them in a state of purity. The results of these attempts have led to very conflicting conclusions respecting the character of these bodies. Some of the so-called pure preparations of ferments have had the properties of the proteids, and have more or less agreed with them in composition, while others have differed widely from the proteids in both respects.

It still seems to be the opinion of many that the enzymes are

[1] Read before the New York Section, December, 1894. Reprinted from the Report of the Connecticut Agricultural Experiment Station, 1894.

in fact true proteids and that the ferments thus far supposed to be obtained in a state of purity were simply somewhat contaminated with other substances. This opinion is based on the fact that all those changes which are ascribed to the action of enzymes occur only in solutions which contain proteid matter, and that the activity of the ferment is greatly influenced by conditions known to have a pronounced action on proteids, such as heat, the presence of acids and alkalies, salts of the heavy metals, etc.

The first discovered and one of the most carefully studied of these ferments is diastase. The practical application of the action of diastase in the manufacture of alcohol and of malt liquors has given rise to careful and extended studies of the conditions affecting the activity of this ferment, and the result of these studies has led some to the opinion that the active substance is the albumin present in the malt extracts. The conversion of starch into maltose and dextrin by diastase increases in rate and extent as the temperature of the solution is raised, until the heat reaches the point at which the albumin begins to coagulate. The ferment then begins to lose power, and, when the heat is sufficient to completely coagulate the albumin, its amylolytic action ceases entirely. In 1883, C. Lintner, Jr., showed that the diastatic power of fifteen different samples of malt was very nearly proportional to the amount of coagulable albumin which they contained. In 1886, however, C. J. Lintner prepared diastase in, as he supposed, a state of purity, and came to the conclusion that the results of his analysis of diastase indicate that, in the ferments, we have a special class of proteid substances. The composition of Lintner's purest diastase differed much from that of the proteids, since it contained only two-thirds as much nitrogen and also less carbon. His diastase furthermore, failed to give the reaction with cupric sulphate and potassium hydroxide which is characteristic of proteid matter. These results of Lintner's threw much doubt on the hypothesis that the vegetable albumin is identical with diastase.

In my investigations of the proteids of wheat, rye, and barley, I found in all these grains the same albumin and was impressed with the close relation between the temperature at which this albumin coagulates and the temperature at which diastase begins

to lose its activity. The aqueous extracts of these seeds, as is well known, possess considerable diastatic power, and it seemed to be more than probable that this was due to the albumin. I accordingly undertook an investigation of this subject, and I now offer the results thus far obtained, which are preliminary to a more extended study.

The usual method of preparing vegetable enzymes is to treat the aqueous or glycerol extract containing them with alcohol as long as a precipitate, having fermentative power appears, to purify this by repeated precipitation from its solution in water, by means of alcohol, and finally to subject the aqueous solution to dialysis to remove salts. This method is wholly unsuited to yield pure preparations, because the precipitate produced by alcohol contains not only a large amount of carbohydrates and salts, but also nearly all of the various forms of proteid matter present in the extract. Lintner employed this method, and there can be no doubt that he obtained a mixture of proteids with other substances which defied all attempts at further separation.

The most rational method (hitherto very little used) is first to separate the proteids from the carbohydrates and other soluble substances by saturating the extract with ammonium sulphate, thereby precipitating the ferment and proteids together, next to remove the proteid existing as globulin, by dialysis, and then, if possible, to separate the albumin and proteoses by fractional precipitation with alcohol. In following this method, a measured quantity of malt extract was saturated with ammonium sulphate, the precipitated proteid matter was filtered out, dissolved in water, and the clear filtered solution made up to the volume of the original extract. This solution was found to have the same diastatic power as before precipitation, thus showing that ammonium sulphate had not injured the diastase. Throughout my work diastatic power has been measured by Lintner's method, which gives a very ready means of accurately comparing different preparations. This method consists in adding to each of a series of carefully measured volumes of the solution containing definite amounts of the diastatic preparation, ten cc. of a two per cent. solution of soluble potato starch, and allowing the ferment

to act upon the starch for one hour at the ordinary temperature of the room. At the end of this time five cc. of Fehling's solution are added to each portion and the mixtures are heated for ten minutes in a boiling water-bath. After the precipitated cuprous oxide has settled, where too little sugar has been formed to precipitate all the copper, the liquids will be blue; if sugar is in excess they will be yellow. The one colorless liquid that should result gives the measure of diastatic power. Lintner represented the value of his most active preparation by 100, and that of the other preparations by figures stating the amount of each necessary to give a complete reaction with Fehling's solution under the above conditions, in comparison with his most active preparation, of which, under the conditions of the test just described, twelve one-hundreths of a milligram completely reduced the five cc. of Fehling's solution.

For the sake of comparison I have measured the activity of my preparations by the same standard, so that a preparation whose activity is given as 200 means that six one-hundreths of a milligram sufficed to give a complete reduction.

As Lintner recommended extracting the malt with water containing twenty per cent. of alcohol instead of pure water, since thereby less foreign matter was removed with the proteid, this procedure was first tried. Fifteen hundred grams of ground air-dried malt, prepared in the laboratory, were treated with three liters of twenty per cent. alcohol, the extract squeezed out in a press, and the residue again treated with another liter of the same dilute alcohol. Three liters of extract were obtained which, after being filtered clear, were saturated with ammonium sulphate. Owing to the presence of the alcohol much less ammonium sulphate was dissolved than by a water extract, and the proteids were consequently incompletely precipitated. The precipitate obtained was treated with water and a considerable quantity of insoluble matter, consisting mostly of globulin, rendered insoluble by contact with the reagents, was filtered out. The solution was saturated with ammonium sulphate, and the precipitate dissolved in water. This clear solution was then dialyzed in water for some days, and after filtering from a slight deposit was dialyzed in alcohol of 0.845 sp. gr. for forty-eight hours.

As the water passed out of the dialyzer faster than the alcohol entered, the solution became concentrated and a considerable precipitate formed. This was filtered out and washed, first with dilute alcohol and afterwards with absolute alcohol, and dried over sulphuric acid. This preparation, 1, when thus dried, dissolved in water with the exception of a not inconsiderable residue. When filtered clear, the solution, on heating, gave an abundant coagulum, and after boiling and filtering out the coagulum, the filtrate gave a strong pink color with cupric sulphate and potassium hydroxide, showing the presence of proteose. The diastatic power of this preparation, in comparison with Lintner's best was eighty-six, but, as it was afterward found to contain a comparatively small amount of ash, the test was repeated with the addition of a few milligrams of sodium chloride and then found to equal 150.

The composition of preparation 1 was as follows:

PREPARATION 1.

	Ash-free.
Carbon	52.55
Hydrogen	6.48
Nitrogen	16.41
Sulphur } Oxygen }	24.56
	100.00
Ash	2.29

These figures indicate that this preparation consisted almost wholly of proteid matter, and the reactions proved the presence of at least three forms; namely, coagulated proteid, albumin, and proteose. This mixture was one and a half times more active than Lintner's most energetic preparation, and contained about six per cent. more nitrogen and one-half as much ash. The composition of the preparation is very similar to that of the coagulated albumin-like body obtained from wheat, rye, and barley, and for which I have adopted the name leucosin. As this albumin has been found to have the same composition, whether coagulated by heat or by alcohol, and as most, if not all of the proteids have identical composition (so far as analysis can show), in the soluble and the coagulated states, it seems probable that

preparation 1 consisted mostly of coagulated and soluble leucosin together with a little proteose.

The filtrate from this preparation on addition of absolute alcohol, yielded a small precipitate, 2, which dissolved wholly in water and gave only a very slight coagulum on heating, but a strong pink biuret reaction, showing it to be mostly proteose. Its diastatic power was only nineteen.

As above stated, owing to the presence of alcohol, saturation of the original extract of malt with ammonium sulphate, precipitated only a part of the proteids. Accordingly the filtrate from this first precipitation was dialyzed for twenty-four hours, so as to remove most of the alcohol, and was again saturated with ammonium sulphate. The resulting precipitate was dissolved in water, filtered from a slight residue, and the clear solution dialyzed until nearly all the ammonium sulphate was removed. The dialyzer was then transferred to alcohol and left for forty-eight hours. The resulting precipitate was then filtered out and treated in the manner before described. After drying, this substance, preparation 3, like preparation 1, consisted of insoluble proteid, soluble leucosin, and proteose. Its diastatic power was 133, and it had the following composition:

PREPARATION 3.

	Ash-free. I.	II.	Average.
Carbon	52.34	....	52.34
Hydrogen	6.73	....	6.73
Nitrogen	15.90	15.92	15.91
Sulphur } Oxygen }	....	....	25.02
			100.00
Ash			0.82

The filtrate from this preparation was next treated with a large quantity of absolute alcohol, and the contained proteid completely thrown down. This substance, preparation 4, dissolved entirely in water; its solution yielded but a trace of coagulum on heating, and when boiled and filtered gave a strong proteose reaction. It contained, ash-free, only 12.02 per cent. of nitrogen, and had a diastatic activity of 11.

These results prove that extraction of the malt with twenty per cent. alcohol is not suited for a subsequent precipitation of the proteids with ammonium sulphate; that otherwise the method is capable of yielding preparations of diastase of high fermentative power, which to a certain extent can be separated into fractions containing the different forms of proteid matter; that the fractions including the greatest amount of soluble albumin have the greatest diastatic power; and that a part at least of the proteose is almost, if not entirely, free from this power.

Another extraction was made on a much larger scale, so that the fractional precipitations might be more numerous, and the fractions examined more closely.

Ten kgms. of malt were exhausted with water and the extract was saturated with pure and neutral ammonium sulphate. The very bulky precipitate was suspended in four liters of water and dialyzed until much of the sulphate had been removed and the precipitated proteid largely dissolved. The solution was then filtered from an insoluble residue consisting mostly of globulin, and the clear filtrate was saturated with ammonium sulphate. The precipitate thus obtained was suspended in 1500 cc. of water and was dialyzed until nearly all the sulphate had been removed and the precipitate mostly dissolved. The globulin contained in the extract was thus largely separated and, after it had been filtered out, the clear solution was dialyzed into an equal volume of alcohol of 0.84 sp. gr. After forty-eight hours the precipitate, number 1, which had separated, was filtered out and set aside for further examination. The filtrate was again dialyzed into an equal volume of alcohol of 0.84 sp. gr., and after forty-eight hours another precipitate, II, obtained. The filtrate was further dialyzed into a rather large quantity of somewhat stronger alcohol, and precipitate III separated, and by similarly treating the filtrate from this, precipitate IV was obtained, the filtrate from which, on adding a large quantity of absolute alcohol, yielded precipitate V. All the proteid in the extract was thus separated. Precipitate I was much contaminated with coloring-matter, II less so, and III was nearly colorless, as were also IV and V.

The approximate weights of each of these precipitates was as

follows: I, thirteen grams; II, eight; III, six; IV, five; and V, three, a total of thirty-five grams.

Precipitate I was treated with water and found to be very largely insoluble. The insoluble matter was filtered out and washed with water, and the clear solution was dialyzed for several days to remove all the salts. No proteid was thus precipitated, and the dialysis was continued in strong alcohol, thereby throwing down all but a trace of proteid. The precipitate, preparation 5, weighed 2.11 grams. After drying, it dissolved in water with the exception of a small residue, and its solution when slowly heated became turbid at 65° and deposited flocks at 70°. After boiling and filtering out the slight coagulum, the solution gave a strong pink reaction with the biuret test. These tests show the preparation to consist largely of proteose. Its composition was as follows:

PREPARATION 5.

	Ash-free.
Carbon	53.16
Hydrogen	7.03
Nitrogen	16.50
Sulphur	1.50
Oxygen	21.81
	100.00
Ash	0.49

With Lintner's test this preparation showed a diastatic power of thirty.

The insoluble residue, remaining after treating precipitate I with water, was thoroughly extracted with ten per cent. sodium chloride solution; what remained insoluble in this menstruum was filtered out and the clear solution dialyzed until free from chlorides. The precipitate thus formed, preparation 6, weighed one and two-tenths grams, and after drying was not soluble in water, but dissolved readily and nearly completely in salt solution, having, as was to be expected, the properties of a globulin. This substance had a very slight diastatic power, and its sodium chloride solution when heated slowly became turbid at 60°, a few flocks appearing at 65°, due to a trace of albumin. Its composition was as follows:

PREPARATION 6.

	Ash-free.
Carbon	53.11
Hydrogen	6.45
Nitrogen	15.78
Sulphur } Oxygen }	24.66
	100.00
Ash	0.75

The filtrate from preparation 6 still contained proteid matter which was separated by dialysis in alcohol. Preparation 7 was so obtained, weighing 1.54 grams, having the same properties as 6, and the following similar composition:

PREPARATION 7.

	Ash-free.
Carbon	53.58
Hydrogen	6.70
Nitrogen	15.87
Sulphur } Oxygen }	23.85
	100.00
Ash	1.43

After extracting precipitate I with water and salt solution a very considerable part still remained undissolved. This was treated with water to remove all the salt, and then with alcohol, and was dried over sulphuric acid. This preparation, 8, weighed eight grams and was quite dark in color. It had the properties of an insoluble form of globulin, being dissolved in one-half per cent. sodium carbonate solution and precipitated therefrom by neutralization. Its composition was nearly the same as that of the two last globulin-like preparations and is probably a so-called "albuminate" derived from that substance. The composition of preparation 8 was:

PRRPARATION 8.

	Ash-free.
Carbon	53.55
Hydrogen	7.01
Nitrogen	15.72
Sulphur	1.23
Oxygen	22.49
	100.00
Ash	1.09

Precipitate II was treated with water and the solution thus

formed was dialyzed in water for several days and then in alcohol for twenty-four hours. A quantity of absolute alcohol was finally added to the contents of the dialyzer, thus completely precipitating the proteid. This preparation, after drying, was almost wholly soluble in water, and when heated slowly its solution became turbid at 60° and deposited flocks at 66°. The amount of proteid thus coagulated was somewhat greater than was given by preparation 5, and its diastatic power was likewise greater, being seventy-five. Analysis showed its composition to be as follows:

PREPARATION 9.

	Ash-free.
Carbon	53.19
Hydrogen	6.71
Nitrogen	16.74
Sulphur	1.38
Oxygen	21.98
	100.00
Ash	0.78

This preparation contained a slight amount of insoluble matter, some albumin and much proteose.

The residue of precipitate II, which was not dissolved by water, was treated with sodium chloride solution and the clear extract dialyzed till free from chlorides, but as no precipitate was produced, the dialyzer was transferred to alcohol when preparation 10 separated, weighing 0.49 gram, and containing, ash-free, 15.18 per cent. of nitrogen. It is probable that this is the same globulin obtained in larger quantity from precipitate I, but less pure. That part of precipitate II which remained undissolved after extracting with water and salt solution, was then washed thoroughly with water and with alcohol, yielding preparation 11, which weighed 5 grams and had the following composition:

PREPARATION 11.

	Ash-free
Carbon	53.51
Hydrogen	6.75
Nitrogen	15.76
Sulphur	1.12
Oxygen	22.86
	100.00
Ash	0.66

These figures show that precipitate II contained less globulin and proportionately more leucosin and proteose than precipitate I and it was accordingly found to be more powerfully diastatic.

Precipitate III was in turn treated with water, the resulting extract filtered clear, dialyzed for several days in water, and then in alcohol, absolute alcohol being finally added in quantity to the contents of the dialyzer. The resulting precipitate, preparation 12, weighed three grams. It was almost completely soluble in water, and its solution when slowly heated became turbid at 55° and flocculent at 60°. The amount of this coagulum was much greater than that yielded by preparation 9. The filtrate from the coagulum gave a strong proteose reaction. The diastatic power was 222, indicating the presence of much more diastase than any of the preceding preparations. Its composition was as follows:

PREPARATION 12.

	Ash-free.
Carbon	52.80
Hydrogen	6.96
Nitrogen	16.09
Sulphur	1.45
Oxygen	22.70
	100.00
Ash	0.59

The residue of precipitate III was digested with salt solution, the filtered extract was dialyzed in water till free from chlorides, and then, as no proteids separated, the dialysis was continued in alcohol. Only 0.28 gram of proteid resulted, which, without correction for ash, contained 12.53 per cent. of nitrogen. This was marked preparation 13, and considered to be impure globulin.

The part of precipitate III still undissolved was washed with water and with alcohol, yielding preparation 14, which weighed 2.87 grams. This had the following composition:

PREPARATION 14.

	Ash-free.
Carbon	53.25
Hydrogen	7.65
Nitrogen	16.12
Sulphur	1.38
Oxygen	21.60
	100.00
Ash	0.55

This preparation has a somewhat higher nitrogen and lower carbon content than preparations 8 and 11, which is probably due to its being a mixture of the insoluble form of the globulin with some insoluble albumin coagulated by the long contact with alcohol to which it had been subjected. This is to be expected, as precipitate III contained relatively more albumin than precipitates I and II.

Precipitate IV was next treated with water, the solution filtered clear, dialyzed for some days in water, and afterwards transferred to alcohol, and the dialysis continued. Absolute alcohol was then added to the contents of the dialyzer, giving preparation 15, weighing four grams. This substance dissolved in water to a nearly clear solution, which, when filtered perfectly clear and heated carefully, became turbid at 50° and gave a large coagulum at 56°. After heating the solution and filtering off the coagulum, a good reaction for proteose was obtained with the biuret test. This preparation had a diastatic power of 600. As this was a much more powerful ferment than any yet produced, its properties were carefully studied and will be described at length later. When analyzed this substance was found to have the following composition:

PREPARATION 15.

	Ash-free.
Carbon	52.50
Hydrogen	6.72
Nitrogen	16.10
Sulphur	1.90
Oxygen	22.78
	100.00
Ash	0.66

It will be noticed that the sulphur in this preparation is a little higher than in the preceding preparations, which is probably due to its containing some sulphate.

The part of precipitate IV which did not dissolve in water was treated with salt solution, but no globulin was extracted. The residue was then washed with water, giving preparation 16, which weighed 0.9 gram and had the following composition:

PREPARATION 16.

	Ash-free.
Carbon	53.42
Hydrogen	7.15
Nitrogen	16.65
Sulphur } Oxygen }	22.78
	100.00
Ash	0.24

The composition of this insoluble product shows it to be probably coagulated leucosin.

A portion of precipitate V, when treated with water, was found to dissolve completely. It was therefore washed with absolute alcohol, yielding preparation 27, which weighed 2.87 grams. The clear solution of this substance when heated became turbid at 50°, and yielded a small coagulum at 58°. Boiled and filtered, a strong pink coloration was given with the biuret test, thus showing it to consist mostly of proteose. The diastatic power of this substance was 60, only one-tenth that of preparation 15. Its composition was:

PREPARATION 17.

	Ash-free.
Carbon	51.21
Hydrogen	6.52
Nitrogen	15.40
Sulphur } Oxygen }	26.87
	100.00
Ash	2.37

The lower nitrogen content of this preparation indicates that the strong alcohol had thrown down, together with the proteids, some non-nitrogenous substances.

Much is to be learned by studying these results which will be of service in future attempts to isolate pure diastase.

In the first place, it is plain that we have in our malt extract a globulin, an albumin, and at least one, more probably two, forms of proteose. I believe the substance soluble in salt solution to be a true globulin, since it so readily assumes an insoluble form, and also because a much larger quantity of the same

body was obtained by extracting with ten per cent. salt solution, the malt residue remaining after the extraction with water. I also think that at least two forms of proteose are present, for the water-soluble portion of precipitate I consisted chiefly of proteose, as did also precipitate V. The amount of proteose diminished from precipitate I to precipitate IV, which contained the least, while precipitate V, which, it will be remembered, was thrown down by adding to the solution a very large amount of absolute alcohol was mainly proteose. A part of the proteose was precipitated by alcohol more readily than the albumin, while another part was less readily precipitated. Beside the albumin, globulin, and proteose, we have also to take account of the "albuminate" or insoluble forms of the albumin and globulin. The results of this extraction show that the globulin is rendered insoluble more rapidly than the albumin, so that precipitation with alcohol and solution in water, repeated a few times, may be depended upon to remove the former. Whether repeated fractional precipitation can be employed to completely separate the albumin from the proteoses is not so certain. The albumin is thrown down from the malt extract by saturation with magnesium sulphate, and it is not unlikely that a complete separation can be accomplished by this reagent. It is, however, not to be forgotten that the diastase may be a substance which, when heated to from 50°–60°, splits apart into an albumin and a proteose, and that the proteose found in the solutions which have been heated is a decomposition product of the diastase. Kühne's attempts to produce pure trypsin led him to suspect that this ferment is a body which, when heated, yields a coagulable fraction and a proteose-like substance. Hammarsten's more recent work on a neucleoproteid obtained from the pancreas also points strongly in this direction.

Now that we have some precise knowledge of the associated substances, it seems probable that we may succeed in obtaining diastase nearly, if not quite, pure, and arrive at a clearer and more positive knowledge of this ferment, and also have a guide in further study of other enzymes, which will lead to a more satisfactory understanding of this whole subject. It is probable that the ferments contained in seeds are much easier to prepare than

those of animal origin, since the substances with which they are associated are largely non-proteid and comparatively easy to separate. It is also certain that the amylolytic ferments present an easier problem than the proteolytic, for the products of the activity of the latter are so similar, in their nature, to that which the ferment is supposed to possess, as to make it always a matter of great uncertainty whether the separated enzyme is free from those bodies or not.

As already stated, preparation 15 was a very energetic ferment, and on this account its properties were more fully studied, with the following results:

Dissolved in water this substance gave all the usual proteid reactions, and when heated slowly became turbid at 50° and gave a flocculent coagulum at 56°. This is exactly the temperature of coagulation of the albuminum (leucosin) which I have prepared from wheat, rye, barley, and malt, with identical composition and properties. The aqueous extracts of these grains have, moreover, a strong diastatic action on starch. The amount of coagulable albumin in preparation 15 was determined and found to be 53.2 per cent. of the dry substance.

These facts point strongly to the albumin as being the diastatic substance, yet there are several facts hard to explain, if this be true, which cannot be overlooked. Although in general the diastatic power of my preparations was greater the larger the amount of coagulable albumin they contained, I have never yet been able to establish any numerical relations between the two. In no case have I found any diastatic action with solutions free from albumin. Furthermore, the activity of my preparation 15 is such as to require a much greater diastatic power for malt than this shows if its coagulable albumin is the enzyme.

A malt extract corresponding to a solution of the diastase in five milligrams of malt had the same diastatic power as 0.02 milligram of preparation 15. As the preparation contained but a little over fifty per cent. of coagulable albumin, this would correspond to only 0.01 milligram of albumin in the five milligrams of malt, or two-tenths per cent. The amount of albumin in malt is much greater than this, as it is also in wheat, rye, and barley, whose diastatic power is greatly inferior to that of malt. It is

not probable that the *separated* diastase is more active than that *in the seed*, especially in view of the experiments which follow, comparing the action of malt extract and preparation 15. The only explanation of this that occurs to me, is that the active diastase is a combination of albumin with some other body, presumably the proteose, which breaks up on heating, yielding coagulated albumin, and that, besides this combined albumin, free albumin is also present, which has no diastatic power, but which is coagulated at the same time. There is no direct evidence, however, that this hypothesis is correct.

Compared with other so-called pure ferments, preparation 15 is very active. At 20° it was in a condition to produce, from soluble starch, over 2000 times its weight of maltose and a further undetermined quantity of dextrin, within one hour. After having been dried over sulphuric acid and kept for six months, its activity was reduced to one-half, but in this condition it produced in seventeen hours, at 20°, 10,000 times its weight of maltose besides an unknown quantity of dextrin. At 45° the same quantity of maltose was produced in one hour as at 20°. At 50° much less and at 55° very little maltose was formed. These tests were made by using an amount of diastase solution just sufficient to produce enough maltose at 20° to exactly reduce five cc. of Fehling's solution.

Compared with malt extract of the same diastatic strength, as measured by the amount of maltose produced in one hour at 20°, the distilled water solutions of preparation 15 have a less powerful action in liquefying starch paste. Five cc. of malt extract added to ten cc. of a starch paste containing two per cent. of starch, dissolved the starch completely in eight minutes, while the solution of preparation 15 required thirty-seven minutes.

The malt extract is also more energetic in converting starch completely into bodies giving no color with iodine. Five cc. of the same malt extract added to ten cc. of soluble starch solution caused the blue reaction with iodine to disappear in thirteen minutes, while it required thirty-eight minutes to reach the same result with the solution of the separated diastase. When, however, the diastase was dissolved in malt extract, whose enzymes

had been previously killed by heating, the difference between the separated diastase and that in the malt extract nearly disappeared.

Two test-tubes were each charged with ten cc. of starch paste. To one tube were added five cc. of fresh malt extract, and to the other the same amount of boiled and cooled malt extract in which had been dissolved a quantity of preparation 15, sufficient to make a solution of the same sugar-producing power as the fresh malt extract itself.

The fresh malt extract liquefied the starch in seven minutes, the mixture of preparation 15 and boiled malt-extract in fourteen minutes, while thirty-seven minutes were required to produce the same result with a distilled water solution of preparation 15. In completely converting starch into bodies giving no color with iodine, the solution of preparation 15 in boiled malt extract gave exactly the same result as the fresh malt extract, showing that the difference first noticed was due to the conditions and not to the ferment.

In view of these results, it seems highly probable that diastase is a true proteid, for if we consider the extremely minute quantity of preparation 15 required to produce large amounts of maltose, it is hard to believe that this action is due to some substance adhering to the proteid to the extent of only three or four per cent. at the most. If such were the case it is also remarkable that the enzyme should adhere in so much greater quantity to the particular precipitate represented by preparation 15 than to any of the other numerous fractions. If diastase, then, is to be considered as a true proteid, it is evidently either an albumin, a combination of an albumin with a proteose, or a proteose. We have seen that those fractional precipitates which consist largely or wholly of proteose have little or no diastatic action, amylolytic power being manifested most strongly in the fractions containing the most albumin, and least in those containing but little, though not in strict proportion to the amount of the albumin. It is to be concluded that the diastatic enzyme is most closely related to the albumin, named leucosin, and it is not improbable that further careful study will show more clearly what this relation is.

NOTE ON THE PURIFICATION OF GLUCINUM SALTS.[1]

By Edward Hart.

Received January 19, 1895.

TWENTY years ago I found glucinum in a clay brought to Dr. Drown's private laboratory, in Philadelphia, for analysis. The experience gained then in making the separation from alumina showed clearly that none of the methods then known gave a satisfactory separation. In dissolving the carbonate we found that alumina also dissolves, and that in treating the oxides with solution of ammonium chloride, alumina as well as glucina dissolves.

In beginning the purification of glucina from beryl, which I have undertaken for a more careful study of the metal and its alloys, I determined, if possible, to prepare it in some other way than by the use of the time-honored ammonium carbonate method which, besides giving a material of doubtful purity, is expensive and tedious. Such a method has been found based on the properties of the mixed sulphates from beryl, and which seems not to have been used for this purpose. Perhaps it will be best to describe the method now used in full, without describing the failures through which the work passed.

The powdered beryl is first fused with mixed carbonates and then ground and washed with water. The powdered mass is then mixed with sulphuric acid and evaporated to make the silica insoluble. The sulphate solution obtained from this material is evaporated and treated with an excess of potassium sulphate. Alum crystallizes out and is purified by recrystallization. The mother-liquor contains the glucinum along with the iron and alkaline sulphates. Potassium chlorate is added in excess, and the solution heated to peroxidize the iron. Sodium carbonate solution is now added, little by little, the solution being boiled after each addition until a filtered sample shows no yellow color. The whole solution is then filtered, and the glucinum which will be contained in the filtrate is precipitated by further addition of sodium carbonate.

[1] Read at the Boston Meeting, December 28, 1894.

The method, of course, depends upon the fact that it is impossible to throw down the glucinum until the greater part of the acid has been saturated, the glucinum remaining in solution as basic sulphate. Iron and aluminum, on the contrary, are easily separated. Some care is needed in order to get rid of the last trace of iron, which persistently remains in solution until the point at which the precipitation of glucinum begins is almost reached.

A sample prepared in this way was perfectly soluble in hydrochloric acid, gave no reaction for iron with potassium ferrocyanide, was completely soluble in an excess of ammonium carbonate and caustic potash. The ammonium carbonate solution gave no precipitate on the addition of ammonium oxalate. The method is exceedingly simple, convenient and cheap, and leaves nothing to be desired.

THE COMPOSITION OF THE TUBERCULOSIS AND GLANDERS BACILLI.

By E. A. de Schweinitz and Marion Dorset.

Received April 30, 1895.

WHILE many examinations of the products of bacilli have been made during the past years comparatively little attention has been paid to a comparison of the proximate and ultimate analyses of the germs themselves that are morphologically different, and produce different pathological changes.

Cramer[1] gives the results and analyses of cholera germs from different sources, and concludes that upon easily assimilable media the composition of the bodies of the same germ from different sources, and which vary in virulence, is about the same. Where, however, the media supply food that is but difficultly assimilable the composition of the bodies of the germs will vary. The comparison which he makes between these and several other species shows a variation which indicates a distinct and characteristic composition for each germ.

We have had occasion to collect large quantities of the tuberculosis and glanders bacilli, and have submitted the germs, grown both on the ordinary glycerol beef broth and on artificial

[1] *Arch. f. Hygiene*, 16.

media, to proximate and ultimate analyses. The results are presented in tabulated form.

The germs were freed by filtration from the culture liquid and the last traces of the soluble products removed by washing either with water alone or with the addition of sodium carbonate. The germs were then dried over sulphuric acid and, just before analysis, were further dried at 100° C. In drying, the germs underwent but slight change of color if they had been thoroughly washed. The analyses were made with the germs obtained from one and the same original culture, but the growths of eight or ten different generations were mixed together to secure an average sample. The artificial media used for the cultivation of the tuberculosis bacillus had the following composition:

Water	1,000 cc.
Glycerol	70 grams.
Acid potassium phosphate	1 gram.
Ammonium phosphate	10 grams.
Sodium chloride	10 "
Asparagin	2 "
Magnesium sulphate	0.2 gram.

In table I are given the determinations of the carbon, hydrogen, nitrogen, phosphorus, sulphur, ash, in column I, calculated upon the weight of the sample dried at 100° C.; in column II, upon the ash free substance. With the exception of the nitrogen there seems to be but little variation in the composition of the germs grown on beef broth or on artificial culture media.

I. TABLE GIVING ELEMENTARY ANALYSES OF BACILLUS TUBERCULOSIS.

	Beef broth.		Beef broth.		Beef broth.		Artificial media.	
	Per cent.		Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.	I.	II.
Carbon	....	....	60.12	62.61	62.98	64.06	62.16	63.35
Hydrogen	9.22	9.60	9.15	9.53	7.39	7.52	9.19	9.36
Nitrogen	7.34	7.64	7.27	7.40	8.04	8.18	8.94	9.14
Sulphur	0.44	0.45	....	....	....	....	0.22	0.23
Phosphorus soluble in dilute nitric acid	0.66	....	0.19	....	....	....	....	....
Phosphorus, total (Carius)	0.77	....	0.83	....	0.87	....	0.66	....
Ash	4.03	....	4.03	....	1.77	....	1.92	....

Table II gives the elementary analyses of the bacillus of glanders. The germs for these analyses were filtered off, washed a number of times with water and cold absolute alcohol and dried.

A comparison of these results with those of the bacillus of tuberculosis shows a great and distinctive variation.

II. TABLE GIVING ELEMENTARY ANALYSES OF BACILLUS MALLEI.

	Beef broth.	
	Per cent.	
	I.	II.
Carbon	41.81	44.89
Hydrogen	5.89	6.20
Nitrogen	14.05	14.81
Sulphur	0.99	1.04
Phosphorus, total (Carius)	1.10	....
Ash	5.18	....

The variations in the composition of these two bacilli is still more apparent in a comparison of the amount of the proximate constituents as shown in tables III, IV, V, and VI. The determinations were made according to the general methods prescribed for such analyses. The nitrogen determinations were made by the Kjeldahl method, and from these results the albuminoids were calculated. The figures reported in the table as cellulose were obtained by treating the residue from the alcohol extract with 1.25 per cent. caustic soda for forty to sixty minutes, washing well, then digesting the residue with 1.25 per cent. sulphuric acid for the same length of time, washing, and drying. The loss by ignition of the dried residue should indicate cellulose.

The presence of cellulose in the organs of tuberculous individuals has been examined by Freund, Dreyfuss, Toyosaku Nishimura, with somewhat discordant results. Freund (*Jahr. d. g. Wiener Aerzte*, **28**, *1886*) treated the organs and blood from twenty-five different cases, first by extracting with ether and alcohol, then with dilute sulphuric acid. In this way there were left behind hard round lumps about the size of tubercles, which, while insoluble in dilute were soluble in strong sulphuric acid. This solution diluted with water and heated gave the reduction test for sugar.

III. BACILLUS TUBERCULOSIS. *Beef Broth 1.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract	39.64	41.29	38.95	40.32	39.29	40.80
Alcohol extract	....	....	....	....	....	....
Albuminoids	45.81	47.31	45.87	47.85	45.84	47.53
Cellulose	6.95	7.24	....	....	6.95	7.24
Ash	4.12	....	3.94	....	4.03	....

IV. BACILLUS TUBERCULOSIS. *Beef Broth 2.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract	...	....	....	....	....	....
Alcohol extract	3.04	3.10	....	....	3.04	3.10
Albuminoids	50.25	51.12	45.43	46.25	47.84	48.68
Cellulose	7.37	7.68	....	....	7.37	7.68
Ash	1.67	....	1.87	....	1.77	....

V. BACILLUS TUBERCULOSIS. *Artificial Media.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I	II.	I.	II.	I.	II.
Ether extract	37.76	37.88	37.98	38.71	37.57	38.34
Alcohol extract	4.69	4.79	4.19	4.28	4.44	4.53
Albuminoids	55.87	57.12	....	....	55.87	57.12
Cellulose	3.82	3.89	5.69	5.80	4.75	4.84
Ash	1.92	....	....	....	1.92	....

VI. BACILLUS MALLEI. *Beef Broth.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract	7.91	8.26	7.67	8.09	7.78	8.17
Alcohol extract	....	....	....	....	....	....
Albuminoids	89.81	94.68	85.71	90.43	87.76	92.55
Cellulose	5.87	6.19	....	....	5.87	6.19
Ash	5.18	....	....	....	5.18	....

Schulze's method was also used. Lungs, spleen, peritoneum, and dried blood were cut up finely and subjected to the action of nitric acid and potassium chlorate, white, round nodules, or a flocculent substance were left behind, which, submitted to analysis, after solution in cupric ammonia and reprecipitation, gave results corresponding to cellulose.

Nishimura[1] used for experiment the lungs and blood of tuberculous cows and also of men. The organs, after being finely divided were extracted with ether and alcohol and then with two per cent. sulphuric acid.

The residue, when treated with strong sulphuric acid, gave a solution that yielded the Trommer sugar test only twice out of six experiments.

Nishimura then tried the alkali method. The material was fused with potassium hydrate in the oil-bath at 180° C., the fusion acidified with sulphuric acid, then made slightly alkaline and allowed to stand until clear. The residue was filtered off and tested for cellulose. By this method, from the lungs of a grown person a slight reaction for cellulose resulted with Trommer's test. The spleen and liver, treated in the same way also indicated cellulose. In two cases from children, lungs, liver, and spleen gave the cellulose test.

How should this cellulose content be present in the organs? The most plausible supposition is the assumption that this comes from the presence of the bacilli themselves, and that the bodies of the latter are rich in cellulose. Upon this assumption Dreyfuss[2] examined several varieties of bacilli, bacillus subtilis, pus bacillus, aspergillus glaucus, and by the fusion method with caustic potash, succeeded in obtaining the reduction and phenylhydrazine tests.

Nishimura, found, however, that other bacilli, *e. g.*, the water bacillus No. 28, did not show the presence of cellulose. He extended his researches to the tubercle bacilli themselves. He made four tests upon the tubercle bacilli from glycerol bouillon cultures using the alkali method, but obtained no reduction. From this he concludes that cellulose is not present in the tubercle bacilli.

In our examination of the tubercle bacilli, as indicated above, the digestion of the residue, after extraction with ten per cent. sulphuric acid gave distinct reduction tests with Fehling's solution. In two experiments Hoppe-Seyler's method, by fusing with caustic potash at 180°, was used. In the one a good reduction test was obtained; in the other the reduction test failed.

[1] *Arch. f. Hygiene*, 21, [1], 52.

[2] *Ztschr. Physiol. Chem.*, 18, [3, 4], 367.

From these tests we would conclude that cellulose is present in the tubercle bacilli, but in very minute amount, which may, in some instances, escape detection by the methods generally adopted. Nishimura thinks that possibly the tubercle bacilli form cellulose when they grow in the body, but not on artificial culture media. The fact, however, that the analyses indicated cellulose, both when grown upon glycerol beef broth and upon the mineral salt cultures, would make it probable that the cellulose is a normal constituent and can be produced by the germ from whatever material it feeds upon.

The proximate analyses of the glanders bacilli show results which are markedly different from those obtained with the tubercle bacilli. While the determination of cellulose by the method of difference would indicate its presence, the fusion with caustic potash, according to the same method adopted for the tubercle germs, and subsequent treatment with sulphuric acid indicates the absence of cellulose. Care was taken in filtering the tuberculosis and glandery germs that they were not contaminated with cellulose from filter-paper. The most of them were filtered through porcelain and then scraped off.

In order to show more clearly the variation in the body composition of different germs the following table is appended which gives results obtained by Cramer and others, with different germs, upon varying media. The change in the nitrogen content is very marked, and while the difference of medium influences this to some extent there is still sufficient variation in the different germs to permit of a possible distinction of species. While the products of germs are invaluable as an aid to identification it would appear that the chemical study of the bodies of the germs and the differences in their proximate constituents, especially albuminoids and fat, and a more distinctive study of the albuminoids might be very useful in aiding classification.

In order to form some idea of the composition of the fat extracted from the tuberculosis and glanders bacilli, the fats were saponified with caustic soda and the fatty acid separated. The quantity of acids obtained, however, was small and it was only possible to make melting-point determinations. From these the acids of the glanders seemed to be oleic and palmitic, those from the tubercle bacilli, palmitic and arachidic acid.

The difference in the fatty acids apparent in these two, and which would probably vary as much in other germs, could doubtless be made of use in classification. This study is being continued further and extended to the hog cholera, swine plague, and allied germs.

	Albuminoids per cent.			Ether and alcohol extract per cent.		Ash per cent.	
Media	1 per cent Peptone agar.	2 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Peptone agar.
Bacilli.							
Pfeiffer's capsule bacillus	66.6	70.0	....	14.06	....	9.10	....
Pneumonia bacillus	71.7	79.8	....	11.3	....	10.36	....
Bacillus of Rhinoscleroma	68.42	76.2	....	9.1	....	9.33	....
Spirillum of cholera	....	64.96	....	....	....	...	30.78
No. 28.....	73.1	79.6	....	17.08	....	7.79	....

	Nitrogen.						
	7 per cent Glycerol beef broth. per cent	7 per cent Artificial media. per cent	5 per cent Glycerol beef broth. per cent	1 per cent Peptone beef broth. per cent	Carbon. per cent	Hydrogen. per cent	Ash. per cent
Tuberculosis	7.34	8.94	....	....	62.98	7.34	1.77
Glanders	....	....	14.05	....	41.89	5.89	5.18
Swine plague ...	....	....	....	11.81	44.57	7.20	12.41

BIOCHEMIC LABORATORY,
BUREAU OF ANIMAL INDUSTRY.

A CONVENIENT FORM OF UNIVERSAL HAND-CLAMP.[1]

BY PETER T. AUSTEN AND W. A. HORTON.

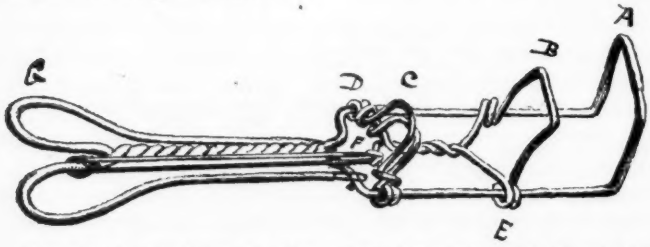
Received April 23, 1895.

THE various holders and hand-clamps used for holding test-tubes and smaller forms belong, as a rule, to two classes. The bite is effected either by a spring or by a pressure exerted by the hand. The difficulty with the first class of holders is that the spring is often inconveniently strong for delicate tubes, and not strong enough for flasks. The second class often fails when long continued holding is involved, as muscular pressure relaxes after a time.

The following little device was worked out to afford a con-

[1] Read before the New York Section, December, 1893.

venient holder that should take from nothing up to a diameter of an inch and a half and yet allow a grasp which corresponds to the weight of the object held, and also not tire the hand, no matter how long it is held.



The clutch B slides on the parallel bars E, and is slightly smaller than the counter-clutch A. This, with its curvature, allows it to grasp any object, no matter how small, that is placed between B and A. A double bearing, to insure ease of movement, is effected by winding the wire at D. The double arch C allows the thumb to press easily and comfortably against it, and act as a knee-joint. The swell G keeps the handle in the grasp, and the rubber strap F brings the traveling clutch back and opens the clamp as soon as the pressure is removed from C.

To use the apparatus, the handle is securely grasped and the end of the thumb is placed against C. On straightening the thumb, in the manner of a knee-joint, the object is tightly held between the clutches. The hand does not tire on continued holding because the pressure is taken in a straight line on the bones of the thumb, and hence calls for so slight a muscular action as to be practically inappreciable.

The clamp is manufactured by Richards and Company.

CHEMICAL LABORATORY OF THE BROOKLYN
POLYTECHNIC INSTITUTE.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. I.]

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received April 22, 1895.

COMMUNICATIONS relating to the electrolytic separation of metals, present in solution as double cyanides, have appeared, from time to time, in this Journal and in other pub-

lications devoted to chemistry, during the past seven years. Thus it was found that in solutions, such as that mentioned, it was possible to separate *cadmium* from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; *mercury* from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; *gold* from palladium, platinum, copper, cobalt, zinc, and nickel; and *silver* from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium. No difficulties were encountered in these separations. About the only objection that could be presented against them, and one that would in any manner postpone their immediate adoption into general analysis, was the fact that from twelve to fourteen hours were required for the deposition of the cadmium, mercury, gold, and silver.

Not more than a year ago Smith and Spencer (This Journal, **16,** 420) observed that the deposition of both mercury and silver was markedly accelerated when the electrolyte undergoing decomposition was heated from 65° to 70° C. It will be recalled that all the earlier separations noted above had been carried out at the ordinary temperature. It appeared, therefore, desirable to further extend the study, and in the lines which follow results are given which were obtained from this new point of view.

While cadmium can be completely separated from its double cyanide solution *in the cold*, the reverse occurs if the liquid be raised to 65°. Thus, in the communication of Smith and Spencer, evidence is given that in a warm solution silver can be fully separated from cadmium, and in the table below it will be observed that mercury and cadmium can be similarly separated. It was, therefore, impossible to review the separations of cadmium from the various metals from which it had been fully separated in the cold. The experiments were accordingly limited to mercury, gold, and silver with several typical metals, as the conditions under which their separation proved successful would doubtless serve for the remaining representatives of the various groups from which separations had been effected.

In the earlier communications it was customary to report the strength of the acting current in cubic centimeters of electrolytic gas per minute. In the present presentation the *normal density* (N. D.) of the current for 100 square centimeters of electrode

surface will be given in ampere units. The reader will also bear in mind that the temperature of the solutions operated upon was, in all cases, 65° C.

MERCURY SEPARATIONS.

Mercury taken. Grams.	Mercury found. Grams.	N. D. of current in ampere units per minute.	Time required for precipitation.	Potassium cyanide in grams.	Cadmium present in grams. per cent.	Zinc present in grams. per cent.	Nickel present in grams. per cent.	Cobalt present in grams. per cent.
0.1901	0.1907	0.02	3 hours.	2	100	100	100	100
.....	0.1903	0.02	3 "	2	100	...	...	...
.....	0.1902	0.06	3½ "	2	...	100	...	...
.....	0.1900	0.06	3½ "	2	...	100	...	...
.....	0.1896	0.06	3½ "	2	...	100	...	...
.....	0.1905	0.08	3½ "	3	...	...	100	...
.....	0.1908	0.08	3½ "	3	...	...	100	...
.....	0.1898	0.08	3½ "	2	...	...	...	100
.....	0.1896	0.08	3½ "	2	...	...	...	100

In ordinary gravimetric analysis it would not be possible for the analyst to separate mercury from any one of the metals just given as completely nor as quickly as indicated in the table.

Gold was separated from cobalt, arsenic, copper, zinc, and nickel, the quantity of gold present in each trial being 0.1087 gram, and each of the other metals in equal amount. But one separation was made with each metal. The quantity of cyanide ranged from one to two grams; the period required for the precipitation of the gold varied from three to three and one-half hours. In all the trials, excepting that with copper, the current was N. $D._{100}$ = 0.1 ampere. In the exceptional case it was reduced to 0.07 ampere. The quantities of gold obtained were:

1..... 0.1084 gram.
2..... 0.1080 "
3..... 0.1093 "
4..... 0.1088 "
5..... 0.1082 "

The separations of silver were limited to zinc, nickel, and cobalt. The quantity of silver was 0.1465 gram and the other metals in equal amount. The quantity of cyanide in all instances was two grams, while the current strength was N. $D._{100}$ = 0.04 ampere. The time of deposition did not exceed three hours. The precipitated silver equaled:

1	0.1464 gram.
2	0.1464 "
3	0.1460 "
4	0.1464 "

The separation of silver from copper and from cadmium is just as rapid and complete as these last separations.

The deposits of mercury, gold, and silver, were carefully examined in the quantitative way for the various metals with which they had been associated; in every instance they showed themselves perfectly pure, so that these methods can be relied upon and trusted where accurate and rapid work is required.

The metallic deposits were washed and dried in the manner described in previous articles.

During the progress of the preceding experiments behaviors were observed pointing toward the separation of silver from gold, and mercury from gold and from silver in cyanide solution, but thus far expectations in these directions have not been realized. When conditions apparently favorable were obtained, traces of one or the other metal would be discovered in the metallic deposit, so that, at this moment, trustworthy and definite data cannot be given.

UNIVERSITY OF PENNSYLVANIA.

ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

BY C. E. LINEBARGER.

Received May 3, 1895.

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12. Relations between the concentrations in the gaseous and liquid phases.
13. Heat of dilution and solution; ideal concentrated solutions.
14. The vapor-tensions of mixtures of acetic acid with benzene and with toluene.
15. The molecular mass of liquid acetic acid and a general method of determining the molecular masses of liquids.
16. Resumé.

1. INTRODUCTORY.

THE investigation of the elastic forces or tensions of vapors emitted by a solution of a fixed substance in a volatile liquid has received much attention, especially within recent years. The impetus for investigations of this kind is, in a great measure, due to the new notions that have been introduced into science in regard to the nature of solutions. The possibility of ascertaining the molecular mass of a substance from a determination of the amount of the depression of the vapor-tension of a liquid, occasioned by its being dissolved therein in known proportions, has induced chemists to study carefully this field of scientific inquiry, which it may truly be said, has been gone over very elaborately.

In the greater part of the work that has been done, both theoretical and experimental, it has been assumed that the dissolved substance is not appreciably present in the gaseous state, and but sparingly present in the liquid state; in other words, the dissolved substance is supposed to be involatile, and the solutions are made dilute.

Now, absolute involatility in any body whatsoever cannot be affirmed; there must always be, at every temperature, some degree of power of assuming the gaseous state, although it may be so slight as to be imperceptible to our senses. Still, for all practical purposes, the assumption of non-volatility in many substances can be admitted, as our means of experimentation are not sufficiently delicate to detect any small amount of volatility.

Although so much has been done on the vapor-tensions of solutions of fixed substances in volatile liquids, comparatively little attention has been paid to the study of the vapor-tensions of mixtures of the volatile liquids; yet this is the general case, of which the restriction that the dissolved substance be fixed

makes only a special application. It must, indeed, be allowed that the consideration of a mixture of vapors, instead of a single one, introduces certain complications into the problem; and this is, perhaps, just the reason so little work has been done on this part of the subject; still difficulties of this sort are probably not unsurmountable.

The limitations of work on vapor-tensions to dilute or, at most, moderately concentrated solutions cannot be said to be satisfactory. True, the theory of solutions has been developed on the hypothesis that dissolved matter, in analogy with gaseous matter, is in a state of considerable dilution; and experimental confirmations of theoretical predictions can be expected only when such a state of affairs is realized. Notwithstanding that circumstance, it seems of importance to extend our line of operations and attack the problems presented by concentrated solutions; perhaps they will be found to exhibit fewer anomalies than has been supposed.

There are two circumstances which render work that has hitherto been done on the vapor-tensions of mixtures of volatile liquids of all concentrations unsatisfactory; they are to be found in the choice of the liquids investigated, and the kinds of vapor-tension measured. The liquids chosen were almost invariably those which are now recognized to be made up of associated molecules; they are just those which exhibit the greatest abnormalities in respect to most of their properties, and it cannot be expected that simple relations, if they exist at all, will be discovered when such liquids are used as material of investigation. All investigators also, almost without exception, have measured only the total pressure of the mixtures of liquids examined, which is the sum of the partial pressures, these, however, being entirely unknown. But more important is it to know the share which each vapor has in the exerting of the total pressure, and only when this is learned can our knowledge of the matter be said to be in any adequate measure complete.

This paper seeks to fill in some degree this gap in the subject of vapor-tensions. The method employed is such as to permit of the specification of the partial pressures of a mixture's components, and also of their concentrations in the gaseous phase. The

choice of the liquids has been made with an eye towards employing those which have been found to be most "normal," so that in the examination of more complex liquids, that is, those consisting of associated molecules, the simplicity to be expected in the phenomena of the former may aid us in getting some light on the possible intricacies of the latter. All the mixtures examined are freely soluble in one another so that no disturbing influence from layer-formation can take place.

In reality, we have before us a case of equilibrium; the equilibrating system consists of two substances, each present in two phases, the liquid and gaseous. We have to ascertain at the points of equilibrium the temperature, the partial pressures of the two substances in gaseous phase, and their concentration in both liquid and gaseous phase.

2. HISTORICAL.

The first paper that I know of which treats of the vapor-tensions of mixtures of liquids soluble in every proportion in one another is by Gustav Magnus,[1] who states that, when to a volatile liquid, such as ether, contained in a barometric vacuum, another less volatile liquid, such as alcohol, be added, the tension of the vapors of both liquids is less than that of the ether alone; the cause of this behavior Magnus seeks in a certain reciprocal attraction on the part of the two liquids. Magnus' paper, being almost the first on the subject, contains, as, indeed, is generally the case with pioneer papers, some important statements, which, through the labors of later investigators, have become generalized into wide-reaching laws; but everything in it is purely of a qualitative nature, no reliable quantitative data being given.

Regnault[2] in the course of his extended investigations on the elastic forces of the vapors given off by liquids, determined at

[1] Ueber das Sieden von Gemengen zweier Flüssigkeiten und ueber das Stossen solcher Gemenge. *Ann. der Phys. u. Chem. Pogg.*, **38**, 481-492. *1836*.

[2] Ueber die Elasticitätskräfte der Dämpfe bei verschiedenen Temperaturen im Vacuo und in Gasen; und ueber die Spannung der Dämpfe aus gemengten oder geschichteten Flüssigkeiten; *Ann. der Phys. u. Chem. Pogg.*, **93**, 537-579, *1854*, and Mêmoires de l' Academie des Sciences, **26**, *1862*. Quatrième Partie: Forces Élastiques des Vapeurs qui sont Émises par les Liquids volatiles, Melangées par Dissolution reciproque on superposés. Troisième Classes: Mélanges binaires des Liquides qui se dissolvent mutuellement en toutes Proportions, 724 and 743.

different temperatures by the static as well as dynamic method, the vapor-tensions of several mixtures of various liquids. Regnault did not pay much attention to the composition and analysis of the mixtures investigated, his object being merely to get a general idea of the relations of the vapor-tensions of the mixtures to those of the compotent liquids. Still there is but a little doubt that the composition of the mixtures is specified with sufficient accuracy to admit of his data being regarded as reliable enough for theoretical considerations and confirmations. In a later section are given his results so rearranged as to furnish some indications of the nature of the phenomenon which they represent. Regnault states in the papers printed in the Mémoires de l' Acadimie that his experiments lead to the same conclusions as those of Magnus; but in the German translation (*loc. cit.*) from the Comptes rendus, he does not seem to have given Magnus this credit, which induced the latter in a paper[1] immediately following that by Regnault, to call attention to his results published some eighteen years before (*loc. cit*). In this last paper by Magnus nothing new is communicated, a considerable part of it being occupied with quotations from his former paper.

Plücker[2] determined by means of Geissler's "Vaporimeter" the composition of the liquid and gaseous phases, as well as the total pressure of the latter, of a system consisting of a mixture of alcohol and water; the work has the stamp of having been done with great care, and the accuracy of the results—rather meager, it must be said—can probably be relied upon.

Bussy and Buignet[3] in the course of their researches on the physical properties of mixtures of hydrocyanic acid and water, made determinations according to the static method of the vapor-tensions of seven mixtures of the above two liquids (page 245 of their memoir). The work, which was carried out at 13.25° is fairly accurate, but the range of concentrations is not extensive enough to permit of utilization of their results.

[1] Ueber die Spannkraft der Dämpfe von Mischungen zweier Flüssigkeiten; *Ann. der Phys. u. Chem. Pogg.*, **93**, 579–582, *1852*.

[2] Untersuchungen über Dämpfe und Dämpfgemenge; *Ann. der Phys. u. Chem. Pogg.*, **92**, 193–220, *1854*: A continuation of this article was promised by the author, but I have been unable to find it and regard its appearance as very doubtful.

[3] Recherches sur lácide cyanhydrique: *Ann. Chim. Phys.*, [4] **3**, 231–263, *1864*.

While the preceding scientists for the most part endeavored to find relations between the tensions of vapors emitted by a mixture, and those given off by its components in a state of purity, Duclaux[1] set himself about to get a knowledge of the relations of the composition of the liquid mixture to that of the vapors emitted. His method consisted in distilling a large quantity (1100 cc.) of a mixture of known composition and collecting several distillates, the composition of which was determined through their surface tensions by means of the "Drop-method." Duclaux, believing, for reasons which he does not state, that simpler relations are to be discovered, if the proportions of the liquids in a mixture be expressed in volumes rather than in weights, communicates results and data, which, as he neglects to give any accurate indications as to the temperature at which and the pressure under which the mixtures investigated by him entered into ebullition, and as to the amount and direction of the change of temperature as the boiling proceeded, it is impossible to put into a shape permitting of comparison with others; the mixtures studied consisted of water and the series of alcohols up to caprylic alcohol, and of water with formic, acetic, and butyric acids.

Wüllner[2] determined according to the static method[3] the vapor-tension of five different mixtures of ethyl alcohol and water at temperature intervals of about 10° from 11.8° to 84.6°; also of two mixtures of sulphuric ether and alcohol at temperature intervals of about 3° from 7.2° to a little over 30°. Wüllner had especially in mind in his work the determination of the variation of constancy of the ratio of the tension of the mixture of vapors to the sums of the tensions of each vapor alone with the temperature; no mention is made of experimental details and of the purity of the liquids experimented upon.

It may be well for the sake of completeness to make mention

[1] Sur les Forces Élastiques Émmises par les Mélanges de deux Liquides: *Ann. Chim. Phys.*, [5] **14**, 305–345. *1878.*

[2] "Ueber die Spannkraft der Dämpfe von Flüssigkeitsgemischen": *Ann. der Phys. u. Chem. Pogg.*, **129**, 353–366. *1866.*

[3] *Ann. der Phys. u. Chem. Pogg.*, **103**, 534–542.

here of Alluard's,[1] Berthelot's,[2] and Brown's[3] work on the boiling points of mixtures of liquids, although little is to be found therein which bears directly upon our subject.

An important experimental as well as theoretical investigation on the subject in question has been made by Konowalow.[4] The method employed was the static, so arranged, however, that the error arising from the change of composition of a liquid mixture due to the evaporation of its components was reduced to a minimum. The determinations were made with mixtures of water with each of the first four members of the series of alcohols, $C_nH_{2n+2}O$, and of the series of acids $C_nH_{2n+2}O_2$ at several different temperatures; the work of Konowalow may be looked upon as very accurate.

Among Raoult's numerous and important publications on the vapor-tensions of solutions, there is one which deserves mention in the history of the vapor-tensions of mixtures of volatile liquids, even if one component of the binary mixtures investigated by him has but a feeble tension of vapor. The paper referred to[5] treats of the vapor-tensions of solutions of turpentine, nitrobenzene, aniline, methyl salicylate, and ethyl benzoate, all almost non-volatile liquids, in ether; the determinations were made at ordinary temperatures by the static method, and are to be considered as remarkably exact. In a later section, the data will be given in a modified form.

In the last five or six years papers by Planck, by LeChatelier, and by Nernst, treating of the theoretical side of the question, have appeared; from their importance as well as for convenience of reference, their contents will be quite fully reproduced.

Max Planck[6] enunciated certain relations between the differ-

[1] "Experiences sur la Temperature d' Ebullition de quelques Mélanges binaires de Liquides que se dissolvent mutuellement en tous Proportions.": *Ann. Chim. Phys.*, [4] **1**, 384-392, *1894*.

[2] "Sur la Distillation des Liquides Mélanges." *Compt. rend.*, **57**, 430 *(1863)*; *Ann. Chim. Phys.*, [4] **1**, 384-392, *1864*.

[3] "On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride": Transactions of the Chemical Society of London. **39**, 304, *1881*.

[4] "Ueber die Dampfspannungen der Flüssigkeitgemischen.": *Ann. der Phys. Wied.*, **14**, 219, *1881*.

[5] "Ueber die Dampfdrucke Atherischer Losungen.": *Ztschr. phys. Chem.*, **2**, 353-373, *1888*.

[6] "Ueber die Dampfspannung von verdünnten Losungen flüchtiger Stoffe.": *Ztschr. phys. Chem.*, **2**, 405-414, *1888*.

ence of concentrations of mixtures of two volatile substances in equilibrating gaseous and liquid phases, and the depression of the vapor-tension, which permit of experimental verification. Planck assumes the applicability of the law of Raoult-van't Hoff and that of Henry to the case of the vapor-tensions of mixtures of volatile substances (liquids); that is, there must be direct proportionality between lowering of vapor-tension and molecular concentration, and also between concentration in liquid phase and partial pressure in gaseous phase; furthermore he states expressly that his deductions are made for the case of dilute solutions only, and that the substances in all phases of a system consist of normal molecules.

Such a system made up of a liquid and gaseous mixture in contact may be represented by the symbol:

$$nm,\ n_1m_1+n'm',\ n_1'm_1',$$

where n and n_1 represent numbers of molecules, and m and m_1 molecular masses; the accented letters refer to the vapor, and the unaccented to the liquid; those written with the subscript have reference to the dissolved substance, those without subscript to the solvent; n and n' are large in comparison with n_1 and n_1'. The numerical concentrations of the individual substances are:

$$c=\frac{n}{n+n_1};\ c_1=\frac{n_1}{n+n_1};\ c'=\frac{n'}{n'+n_1'};\ c_1'=\frac{n_1'}{n'+n_1'}.$$

If a reaction supervenes occasioning the following changes in the numbers of the molecules:

$$\delta n:\delta n_1:\delta n':\delta n_1'=\gamma:\gamma_1:\gamma':\gamma_1',$$

equilibrium occurs, in case this condition,

$$\gamma\log c+\gamma_1\log c_1+\gamma'\log c'+\gamma_1'\log c_1'=\log K,$$

is fulfilled[1]; K is a function of pressure and temperature. In the case before us, we have two different reactions to consider: the vaporization of the solvent and that of the dissolved substance. Accordingly:

1. $\gamma=-1\quad\gamma_1=0\quad\gamma'=1\quad\gamma_1'=0$
2. $\gamma=0\quad\gamma_1=1\quad\gamma'=0\quad\gamma_1'=1$

The necessary conditions for equilibrium are:

[1] See M. Planck. Ueber die Vermehrung der Entropie. *Ann. der Phys. Wied.*, **32**, 489. *1887.*)

$$-\log c+\log c'=\log K$$
$$-\log c_1+\log c_1'=\log K_1,$$

or, if it be taken into consideration that c and c' differ but little from unity, and if members of higher degrees be neglected:

$$c_1-c_1'=\log K,$$

and

$$\log\frac{c_1'}{c_1}=\log K_1.$$

Only the first of these relations can be gotten into a form experimentally verifiable in the present state of our knowledge, and, accordingly, it alone will be treated of in this review.

K is not a directly known function of temperature and pressure, and in order to get its expression in terms of those energy-factors, use must be made of the thermodynamic differential equation:

$$\frac{\delta(\log K)}{\delta p}=-\frac{V}{T}.$$

V being the change of volume occasioned by the reaction at the temperature T, $\log K$ developed in a series according to powers of $(p-p_0)$ becomes:

$$\log K=\log K_0+(p-p_0)\left(\frac{\delta\log K}{\delta p}\right)_0+\cdots\cdots\cdots$$

The subscript $(_0)$ indicates that for p the value p_0 is to be placed; on account of the great dilution, $(p-p_0)$ must be small, and hence all terms in the series can be neglected after the first power. If the term $\frac{V_0}{T}$ be substituted for the differential quotient, the equation

$$c_1-c_1'=\log K_0-(p-p_0)\frac{V_0}{T}$$

is obtained.

V_0 is the change of volume of the system, when, at the temperature T and under the pressure p_0, a gram molecule of the solvent vaporizes; accordingly we can put for it the molecular volume of the vapor, which is equal to $\frac{T}{p}$ by Boyle's and Gay-Lussac's laws; we then obtain

$$c_1-c_1'=\log K_0-\frac{p-p_0}{p_0}.$$

K_0 depends only on the temperature and remains constant during isothermal changes of pressure. If we take $p=p_0$, we have to do with the pure solvent, and c_1 and c_1' must be equal to zero, as well as log K also; and generally we may put

$$c_1 - c_1' = \frac{p_0 - p}{p^0}.$$

In words this relation runs thus: "The relative depression of the vapor-tension is equal to the difference between the concentrations of the dissolved substance in the liquid and in the vapor."

Planck also got another expression for the differences between the concentrations $(c_1 - c_1')$ in the following manner: If the equation $c_1 - c_1' = \log K$ be developed in a series according to the powers of $T - T_0$, the series

$$\log K = \log K_0 + (T - T_0)\left(\frac{\delta \log K}{\delta T}\right)_0 + \cdots\cdots$$

is obtained. Treating this equation in a way similar to that taken in the previous case, and making use of the thermodynamic relation,

$$\frac{\delta(\log K)}{\delta T} = \frac{Q}{T^2},$$

we obtain the expression

$$c_1 - c_1' = (T - T_0)\frac{Q}{T_0^2}$$

where Q is the heat which is derived from the exterior, when a gram-molecule of the solvent vaporizes at the temperature T_0 and under the pressure p. Planck accordingly enunciates this law: "The difference in the concentrations of the dissolved substance in the liquid and in the vapor is equal to the rise in the boiling point, divided by the square of the boiling point and multiplied by the molecular heat of vaporization of the solvent."

From experiments by Konowalow (*loc. cit.*) on mixtures of formic acid and water and of isobutyl alcohol and water, Planck calculated, according to his two formulas just given, the concentration in the gaseous phase, a satisfactory correspondence between the two sets of data being found.

Le Chatelier[1], in his remarkable paper on chemical equilib-

[1] Recherches Experimentales et Thèoriques sur les Equilibres Chimiques: Extrait des Annales des Mines de Mars-Avril, *1888*, 281.

rium, devotes a section to the theoretical treatment of the vapor-tension of a mixture of liquids. The expression finally arrived at is quite complicated, and, although important results may be probably obtained by its applications, it is not expedient to enter into its development here.

A. Winkelmann[1], in seeking experimental proof of the relations established by Planck (*loc. cit.*) between the composition of liquid mixtures and their vapors, condensed some of the vapors arising from a solution and ascertained the composition of the condensed vapors, or liquid by measuring its index of refraction. The experiments were made with mixtures of water and propyl alcohol; there is undoubtedly a correspondence between his experiments and Planck's theory, but it cannot be said to be very close.

Nernst[2] also has found an expression for the concentration of a volatile dissolved substance in the gaseous phase in terms of vapor-tensions. If n be the number of molecules of dissolved substance contained in N molecules of a solvent, k a factor of proportionality corresponding to the absorption coefficient of the dissolved substance, and p the partial pressure of the vapor of the dissolved substance in the saturated vapors over the solution, by Henry's law, the equation

$$Kp = \frac{n}{n+N}$$

may be formed. The vapor-tension of the solvent P is

$$P = P_0 \frac{N}{N+n}$$

where P_0 is the vapor-tension of the pure solvent at the temperature in question.

According to Dalton's law, the total pressure of the saturated vapor π of the solution is

$$\pi = P + p$$

[1] Ueber die Zusammensetzung des Dampfes aus Flüssigkeitgemischen: *Ann. der Phys. Wied.*, **39**, 1–15, *1890*.

[2] Vertheilung eines Stoffes zwischen zwei Lösungsmittel und zwischen Lösungsmittel und Dampfraum: Dampfspannungen verdünnter Lösungen flüchtiger Stoffe *Ztschr. phys. Chem.*, **8**, 124, *1891*.

and the composition of the vapor may be shown to be

$$K\frac{n'}{N'+n'}=\frac{p}{P+p}.$$

Where N' and n' have the same significance for the vapor as N and n have for the liquid mixture.

Nernst gives in a little table a comparison of the data calculated by his formula with those obtained by the use of Planck's formula, both in turn being compared with the results of Winkelmann's experiments.

TABLE I.

Mixture of 6.2 grams propyl alcohol and 93.8 grams water.

						Per cent alcohol in vapor.		
t	$P_0 t$	π	P	p	$\frac{n'}{N'+n'}$	Winkelmann.	Nernst.	Planck.
17.65	15.0	20.8	14.7	6.1	0.293	....	58.0	64.2
31.5	31.3	....	30.7	....	....	52.3	59.4	66.0
40.3	55.7	79.4	54.6	24.8	0.312	57.4	60.2	67.2
51.0	96.7	138.7	94.8	43.9	0.316	60.8	61.9	67.7

It is apparent that Nernst's calculated data correspond better with the data observed than do those calculated by Planck's formula, although the correspondence in no case can be reckoned very close; it must be kept in mind, however, that Winkelmann's method is not very exact, and that the vapor-tensions and composition of distillates have been measured on chemical preparations from different sources. A difference, which may be called an advantage, between Nernst's and Planck's formulas, is that the former is not, like the latter, restricted to the consideration of dilute solutions only.

Nernst has also developed certain views in regard to the vapor-tensions of binary mixtures of volatile liquids.[1]

Taking as base of his considerations the empirical law: the vapor-tension of a liquid is lowered when a foreign fixed substance is dissolved in it; he states that this law is applicable also to solutions of volatile substance, only, in this case, the superincumbent vapor consists not of that of the solvent alone, but of a mixture of those of the dissolved liquid and of the solvent; the gaseous phase of the system contains both components of the so-

[1] *Theor. Chem.* 97, *1893*, and Siede und Schmelzpunkt, 67, *1894*.

lution, and according as the partial pressure of one component is greater or less than the diminution of the vapor-tension of the other which it causes by its presence, the total tension of the solution is greater or less. If now a small quantity of a liquid, A, be added to a liquid, B, the vapor-tension of B will be diminished proportionally to the quantity of A added; but the total pressure of the resulting solution will be increased, inasmuch as A as well as B gives off vapors, and the partial pressure of A is so much the greater as the solubility of the vapor A in the solution is smaller. According as the first or the second influence preponderates, the vapor-tension of the solution will be smaller or greater than that of the liquid B in a state of purity. Since the properties of such a mixture must vary continuously with the composition, the influence of the proportions of the two liquids upon the vapor-tension of the mixture may be considered under three cases.

1. The vapors of both A and of B are easily soluble in each other. If we add ever-increasing quantities of A to B the vapor-tension of the mixture will at first sink to a minimum and then rise, until, when a very great quantity of A has been added, it will approximate to that of the liquid A in a state of purity.

2. The vapors of A and of B are but slightly soluble in each other. If constantly increasing quantities of A be added to B, the vapor-tension increases, reaches a maximum, and decreases when a large excess of A has been added, to that of the pure liquid A.

3. The vapor of A is easily soluble in B, while the vapor of B is but slightly soluble in A. The addition of constantly increasing quantities of one liquid to the other causes the vapor-tension of the resultant mixture to pass without maximum or minimum from the vapor-tension of the second liquid to that of the first. But it is perhaps possible that the vapor of B in A is so difficultly soluble that the addition of a small portion of B to A elevates the vapor-tension, while at the same time the vapor of A is so easily soluble in B that by addition of A to B the vapor-tension is lowered. In that case, when B is added to A the vapor-tension increases at first, passes through a maximum, decreases to pass through a minimum, finally rising and approximating, when great excess of B is present, to that of the pure liquid B.

Recently, George U. A. Kahlbaum[1] and his assistants have determined according to the dynamic method the vapor-tensions at different temperatures of mixtures of water with formic and with acetic acid; also of mixtures of various acids of the fatty series. The determinations, which are very numerous, have been made by a method and with material undoubtedly capable of giving the best of results; it is to be regretted, however, that associated, instead of normal, liquids were taken.

It is seen in the foregoing historical sketch that only in the rarest cases have mixtures of normal liquids been investigated as to their vapor-tensions, and the partial pressures of the constituents of the vapor been determined. Now, as already stated on page 617, in order to get a full knowledge of the phenomena of vaporization of mixtures of volatile liquids, we must learn what the partial pressures of each is, when converted into vapor in equilibrium with the liquid phase; and we are the more likely to get clear ideas by investigating the simplest mixtures first, that is, mixtures made up of simple normal molecules. Having by considerations similar to these been led to take normal liquids to form the mixtures, the vapor-tensions of which are to be determined, my first task was to devise some experimental method, which furnishes a means of measuring the partial tensions of the vaporous members of a system of bodies. In order to do this, it is almost indispensable that the composition of the vapor be known, for, that being the case, it is easy to determine what part of the total pressure is to be attributed to each of its components. The problem then reduces itself to one of a simple analysis; but the difficulty is to get the vapor away from the liquid with which it is in equilibrium without its composition becoming changed during the operation. If the so-called static method of determination of vapor-tensions be adopted, it is possible by enlargement of the barometric vacuum to be filled by the vapor, and, after equilibrium has been attained, by separation of the liquid from the vapor by means of a stop-cock or other arrangement, to get enough of vapor to permit of its analysis. But a small amount can be obtained, however, and there is

[1] Studien über Dampfkraftmessungen. Basel, *1893*.

great danger that the composition of the liquid mixture becomes considerably changed.

It is possible to collect some of the condensed vapor given off by a boiling mixture of liquids, and determine its composition, as did Duclaux in the paper cited above (page 620). Here, although it is easy to get a sufficient quantity of the condensed mixture of vapor to permit of quite accurate analysis,—provided that a method of analysis of the two liquids in question had been elaborated,—the change of concentration of the solution during the boiling as well as the concurrent change of temperature, together with the other disturbing circumstances, render the accuracy of such work rather illusory.

Accordingly, another means of determination of vapor-tensions had to be found for the purpose of this investigation; and, indeed, the method founded upon the determination of the quantity of a volatile liquid carried off by a definite volume of an inert gas made to pass through it, and the direct subsequent analysis of the gaseous mixture, either by passing it through appropriate liquid absorbents, such as an alkali, where one of the components of the gaseous mixture is an acid, or over decomposing agents, such as red-hot lime, etc., in case one of the components contains sulphur or a halogen, has been adopted; the method, be it said right here, has been found to meet the requirements of the investigation in a satisfactory manner. It is, indeed, true that the variety of the liquids which can be subjected to investigation is limited, for one member of a mixture must needs be a liquid containing a halogen or sulphur atom, or an acid. Still it is possible to find enough such liquids of differing functions that the results obtained by them can without question be transferred to mixtures made up of any normal liquids whatsoever, and any conclusions drawn, become general.

3. DESCRIPTION OF APPARATUS.

It is of prime importance in the determination of vapor-tensions that the temperature be kept uniform; accordingly I describe, first of all, the apparatus employed for that purpose.

Thermostat.—This consisted of a cylindrical copper vessel holding nearly forty liters of water. It was heated by means of

a ring burner; the pressure of the gas was kept constant by means of a pressure-regulator, and a thermo-regulator as described by Ostwald,[1] controlled the combustion of the gas. To insure uniformity of temperature in all parts of the bath, the water was kept in constant agitation by means of a number of fine streams of air blown up through it, the laboratory being provided with air under pressure. Such a means of agitation gives very satisfactory results; it takes up but very little room, and permits of the examination of the pieces of apparatus plunged in the water by shutting off for a few seconds the flow of the air.

The temperature of the bath remained constant to within 0.05° during an experiment; the thermometer employed was one graduated to tenths of degrees, and had recently been tested by the "Physikalische Reichsanstalt" of Berlin.

The apparatus consisted of three principal parts, each made up from material easily found in almost every chemical laboratory. The first part consists of those pieces required to measure a definite volume of air, to compress it enough to force it through the apparatus, and to dry it thoroughly; the second part is the contrivance for saturating the volume of air with the vapor of the liquid under examination; and the third is the arrangement for the analysis of the gaseous mixture.

First Principal Part of Apparatus.—This consists of a measuring vessel, a vessel for regulating the internal pressure, a manometer, and a system of drying-tubes. I pass to the description of each.

The Measuring Vessel consists of an ordinary bottle of a capacity varying from one to three liters, according as it is required to employ a larger or a smaller volume of air; the height of the bottle should be such that only the neck is above the water; in its neck is fitted a good rubber stopper through which passes one branch of a T tube. This branch of the T tube is made of tubing of about a quarter inch bore, and is about eight inches long, while the other branch has only half this bore, with a length of about three inches. The wider branch of the tube is

[1] *Ztschr. phys. Chem.*, **2**, 565, *1888*.

pushed through the stopper so that its lower edge is just flush with that of the rubber, and care is taken that this adjustment is in every experiment maintained, as well as that the stopper is always inserted to the same distance in the neck of the measuring vessel. In the upper end of the wider branch of the T tube is inserted (an air-tight joint being assured by the use of rubber tubing) a tube somewhat drawn out and narrowed at its lower end, and provided with a stop-cock at its upper end. The end of the lower part must be about a half inch above level of the stop of the measuring vessel, and the upper end is put, by means of a piece of rubber tubing, in communication with a water supply at constant level about a yard above the thermostat. If the stop-cock be opened, water will flow into the vessel, and displace the air therein contained which escapes through the side branch, which, being in the middle of the vertical branch, is an inch or so above the orifice of the tube introducing the water.

Sufficient mercury is poured into the vessel to make it sit firmly on the floor of the thermostat. The residual volume of the vessel is carefully determined by pouring into it from graduated vessels, enough water to fill it up to the level with the upper surface of the stopper. If the adjustment of the stopper and the tubes be always the same, duplicate determinations of the capacity do not differ by more than one-half cc. If the same volume of mercury always be taken, the volume of water will represent the volume of air passed through a liquid or mixture of liquids undergoing investigation in all determinations.

It is superfluous to make corrections for the expansion of the mercury and the glass when determinations of vapor-tensions are made at higher temperatures, as the error of the estimation of the capacity exceeds the amount of the corrections.

The Pressure Regulator consists of a bottle of any convenient size, provided with enough mercury to make it stand steadily under water, and fitted with a twice perforated rubber stopper. Through one of the holes of the stopper passes a tube nearly to the level of the mercury and furnished with a stop-cock at its upper end; this tube is connected by means of rubber tubing with the same water source as the measuring vessel. In the other hole is fitted a T tube, of which one of the horizontal

branches is connected by means of a bit of stout rubber with the narrower branch of the T tube belonging to the measuring vessel, while the other is attached by rubber tubing to the other parts of the apparatus. If water be run into the bottle serving as pressure regulator, the air in it is compressed until it can force itself through the liquid with the vapor of which it is to be saturated.

The Manometer is intended to measure the amount of this compression or the internal pressure; it is made of ordinary glass tubing bent into U shape, with the branches about two feet long. It may be put between the measuring vessel and the pressure-regulator, or between the drying tubes and the latter; I have found it most convenient, however, to melt it into the vertical branch of the T tube of the measuring vessel just opposite the horizontal branch, as shown in Fig. 1. The manometric liquid is water, and the differences of the heights of the liquid columns of the two branches, is read to a millimeter by means of a metric rule; the readings are then easily exact to a tenth mm. of mercury.

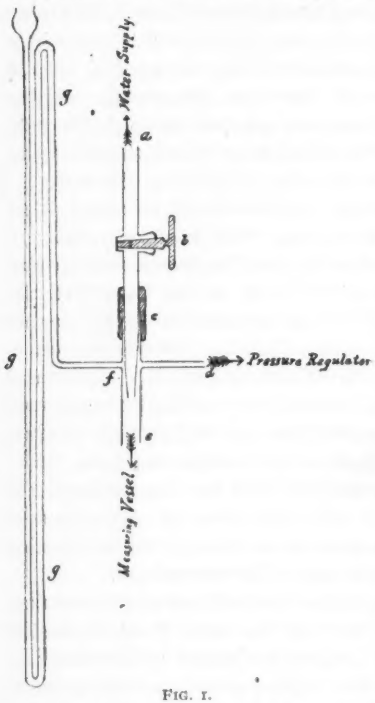

FIG. 1.

The Drying Tubes can, of course, be of various shapes and filled with various drying agents. Liquids, such as strong sulphuric acid, must be rejected, however, as they increase the internal pressure, and often cause an irregularity in the flow of the gas. I found U tubes to be the best shape, and grains of

pumice stone, soaked in concentrated sulphuric acid, the best drying agent; a length of at least sixty centimeters is to be taken, and the pumice must be changed often. When it becomes necessary, in work on acid solutions, to remove the carbon dioxide from the air, an additional tube filled with soda lime is taken. At the end of the last U tube, a mercury valve is attached to prevent the backward diffusion of the vapors; this is of the smallest size convenient, and the delivery-tube dipping into the mercury of capillary dimensions.

Second Principal Part of Apparatus. This is the absorption vessel, which may consist of a simple potash bulb according to Mohr. I found it better, however, to add two more bulbs, making five small and two large ones. As liquids which dissolve rubber somewhat were often introduced into the apparatus, and as it was necessary to let it stand sometime before weighing, the outlet and inlet tubes were provided with tiny ground glass stoppers. At first the bulbs were shut up in a copper case set in the thermostat; the case had holes in its sides, below the surface of the water, for the conduction and abduction of air, platinum capillaries and ground glass caps being employed to make the connections. This arrangement was not, however, found satisfactory, since one was never sure, air being such a bad conductor of heat, that the contents of the bulbs had the same temperature as that of the bath. Also, the platinum tubes proved to be very delicate, breaking readily if bent often, which was inevitable. It was accordingly found best to plunge the absorption vessel directly into the water of the bath, connection with the system of drying tubes being made with a bit of stout rubber tubing of small bore. When the vessel was removed from the water it was carefully wiped dry and set in the balance case, the atmosphere of which was kept dry by means of concentrated sulphuric acid.

Third Principal Part of Apparatus.—In order to analyze the mixture of vapors issuing from the absorption vessel two modifications of this part of the apparatus are required—one to be employed when the gaseous mixture contains a halogen compound of carbon, and the other when it contains an acid. In the first, the compound was decomposed by heated lime, and, in the sec-

ond, the acid was absorbed by a solution of potash or baryta. In the following lines a description of each is given:

(1) The outlet tube of the absorption apparatus is fitted by means of a good cork into one branch of a U tube of rather thick glass; this branch is bent at right angles at about the middle of its length, while the other branch is left straight. The latter branch is held clamped to a heavy and hence steady retort-stand set beside the thermostat, and is connected by means of a narrow lead tube to a tube of hard glass placed in the gutter of a combustion furnace. In the further end of the hard glass tube, a Maquenne absorption apparatus, containing a little dilute nitric acid, is inserted, the connection being made with a rubber stopper; this outlet of the absorption apparatus is in communication with a suction pump, and in the rubber tube making this connection a T tube is interposed, over the open end of which is slipped a piece of rubber tubing long enough to reach to the thermostat. When this tube is open, the interior of the apparatus, up to the liquid in the absorption vessel, is under atmospheric pressure; if it be pinched together a little so as to prevent enough air to feed the suction pump from entering, the pressure in the apparatus may be made less than that of the atmosphere; by this little device it is possible to regulate the pressure with great nicety.

(2) This analyzing apparatus consists simply of a potash bulb, according to Liebig, made of thick glass; one branch is flared out to receive the outlet tube of the absorption vessel, and the other is straight so as to glide up and down in a clamp of a retort stand.

The pieces of apparatus just mentioned will receive complementary description in the directions for performing experiments.

Performance of an Experiment when the Mixture Contains an Organic Halogen or Sulphur Compound.—The hard glass tube (about eighty cm. long) is filled with lime or sodium carbonate just as in a determination of halogens in organic analysis, joined to the lead tubing which establishes communication with the U tubes held in a clamp just above the surface of the water in the thermostat, and placed in the furnace. The gas is now lighted and the tube with its contents heated up to a red heat, while a

current of dried air is passed through it to remove all moisture.

The measuring vessel, the pressure-regulator, and the system of drying-tubes are joined air-tight together, and so set in the thermostat that as much room as possible is left for the absorption vessel.

The absorption vessel is filled with the liquid or solution under examination, a few bubbles of air drawn through so as to get the liquid beforehand in the right position, and carefully weighed. It is then connected with the U tube (of course, no air is now being passed through the analyzing tube), and after a couple of minutes of half submersion in the bath, it is attached to the system of drying tubes. It is now wholly submerged in the bath and air is made to pass through it as follows:

The stop-cock of the pressure-bottle is opened so that water may be run in slowly and, by compression of the air, gradually increase the internal pressure. As soon as bubbles of air commence to pass out of the absorption vessel, the stop-cock of the pressure-regulator is closed, and that of the measuring vessel opened. The water issues in drops or a fine stream in full sight of the operator, and its rapidity of flow can be very easily regulated. Experience has taught me that about a liter an hour was about the best rate; after a brief acquaintance with the apparatus, it is possible to judge very closely from the rate of the flow how long it will take for the measuring vessel to become filled. While the operation is proceeding, the height of the manometric column is read off at several different times; if the rate of flow is constant this does not vary by more than one or two mm. of water, or less than one-tenth mm. of mercury.

The barometer is also read off at the beginning and at the end of the experiment; in all my determinations, the difference of the two readings was less than one mm. of mercury.

A minute or so before the measuring vessel is full, the absorption bulbs are lifted out of the water enough to bring the end tubes about two inches above the surface, and there, together with the joining tube on one side and the cork and end of U tube on the other, are carefully dried with filter-paper. When the water in the measuring flask has reached the mark on the T tube (level of cork), the absorption vessel is detached from the dry-

ing tubes, and the little glass stopper fitted into its inlet tube. Immediately after this operation, the connection between the absorption vessel and the U tube is broken, and as soon as this is done a perforated cork, through which passes a narrow glass tube so bent at right angles that a long vertical branch is obtained is fitted into the U tube, its object being to prevent the escape by diffusion of any portion of vapor contained in the U tube. A current of air is now drawn through the tubes, slow at first to avoid causing too much vapor to pass over upon the heated lime all at once, as, if there be a deficit of air, the combustion is incomplete, and free carbon collects in the cooler portion of the tubes; in a well conducted experiment, the lime should remain perfectly white. Towards the end of the determination, a more rapid stream of air is drawn through the apparatus, so that one may be sure that all the halogen compound has been brought into contact in the decomposing agent. If any free carbon collects in the tube or if the dilute nitric acid in the Maquenne absorption bulb shows on the addition of silver nitrate the slightest trace of cloudiness, the determination ought to be rejected as untrustworthy.

The absorption vessel, as soon as possible after its removal from the water in the thermostat, should be closed with the second tiny stopper, wiped dry, and set in the balance case, where it takes on the temperature of the room. When this is thought to have taken place, it is weighed, and the loss of weight set down as the evaporated quantity of solution. When the furnace has cooled down, the lime tube is removed and its contents washed out with water and nitric acid into a flask, which is set over a flame and boiled until complete solution ensues, more nitric acid being added, if necessary. If more than a half gram of the halogen compound has evaporated, the solution is brought to a certain volume and an aliquot portion of it taken for analysis.

Most of the analyses were made by the gravimetric method of determination of halogens by precipitation with silver nitrate; some, also, were analyzed volumetrically, Volhard's method being employed.

Performance of an Experiment when the Mixture contains an Acid.—The absorption vessel is filled with the mixture being

investigated, and weighed as described above. It is then joined by means of a good cork to the analyzing apparatus, into which are run from a pipette ten cc. of a stock solution of potash or baryta; the pipette being provided with a straight calcium chloride tube filled with soda lime, all contamination from the carbonic acid of the breath is avoided. The alkaline liquor is of such strength that it is more than sufficient to neutralize the vaporized acid. The further end of the analyzing arrangement is closed with a U tube filled with soda lime so that the alkaline solution may be in contact with an atmosphere free from carbon dioxide.

The two pieces of apparatus thus filled and joined together are submerged in the water of the thermostat, the whole being held in place with a clamp embracing the upright tube of the analyzing contrivance and attached to a heavy retort stand. The other end of the absorption vessel is then placed in communication with the drying tubes, etc., by means of a short bit of stout rubber tubing.

The internal pressure is regulated and the air passed just as described in the preceding section, note being taken of the amount of internal pressure, the volume of the air and the barometric height. A slight correction has to be made to the barometric reading for the following reason: after the air passes the liquid contained in the absorption vessel and comes into the analyzing tube, it is under a pressure equal to that of the atmosphere plus that due to the weight of a column of liquid corresponding to the difference of level between the two surfaces of the alkaline solution; this, in my apparatus, was determined to be equal to one mm. of mercury, which was added to all barometric readings.

When the measured volume of air has passed through the apparatus, the stop-cock, through which water enters into the measuring vessel, is closed, the absorption and analyzing vessels are lifted nearly out of water, and after the joint between the absorption vessel and the system of drying tubes has been wiped dry, it is broken. Both the pieces of apparatus are wiped dry with bibulous paper, and agitated somewhat so that any acid vapors in the bulbs may be brought in contact with and absorbed by the alkaline liquor.

The pieces are then disconnected, the absorption vessel stoppered and set in the balance-case, while the contents of the analyzing vessel are poured into a beaker, rinsing being done with water free from carbon dioxide. Without delay, the excess of alkali is estimated by titration against deci-normal acid solution, and by a simple calculation, the quantity of evaporated acid is obtained.

4. CALCULATION OF RESULTS.

In the calculations it is assumed that the laws of perfect or ideal gases may be applied to the mixtures of vapors; that is, the laws of Boyle, Gay Lussac, and Dalton. Where not too much vapor is present in the gaseous mixture the legitimacy of this assumption is unquestionable; and even though this condition be not fulfilled, the approximation to accuracy may be sufficient (see section 6).

Calculation of Volume of Air Passed Through a Mixture.—In order to force the air in the measuring vessel through the liquid in the absorption vessel, it is necessary that it be brought under a pressure equal to that of the atmosphere plus that required to vertically displace the liquid contained in the bulbs, the latter pressure varying with the density and amount of the mixture. The volume of the air under atmospheric pressure may be obtained then as follows:

Let P represent the pressure of the atmosphere. Let P' represent the pressure which forces the air through the liquid. Let V' represent the volume of air under the pressure $P+P'$. Let V represent the volume of air under the pressure P.

According to Boyle's law, and inasmuch as the temperature remains constant,

$$V=\frac{(P+P')\,V'}{P}$$

Calculation of Composition of Mixture of Liquid Vaporized.—As this calculation is simply one of quantitative analysis, it is not necessary to treat of its details.

Calculation of Partial Volumes of Mixtures of Vapors.—Let m represent the quantity of one component in the gaseous mixture. Let M represent its molecular mass. Let 22.32 represent the volume in liters of a gram-molecule of hydrogen at the tem-

perature 0° and under the pressure 760 mm. Let α represent the coefficient of expansion. Let v_1 represent the volume of vapor at the temperature of the determination t and under the atmospheric pressure p. We then have

$$v_1 = 22.32 \frac{m}{M} \times \frac{760(1+\alpha t)}{p}.$$

Calculations of Partial Pressures of Components of Vapor Mixture.—Let v_1 represent partial volume of one component. Let v_2 represent partial volume of the other. Let v represent partial volume of air. Let p_1 represent partial pressure of one component. Let p_2 represent partial pressure of the other. Let p represent the atmospheric pressure.

In accordance with Dalton's law,

$$p_1 = p \frac{v_1}{(v+v_1+v_2)}$$

and

$$p_2 = p \frac{v_2}{(v+v_1+v_2)}.$$

5. DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In order to make a just estimate of the degree of accuracy attainable by the above described apparatus, it is necessary to consider somewhat in detail the possible sources of error that may accompany a determination of the vapor-tension of a liquid made by it.

Error in Measurement of Volume of Air Passed Through the Absorption Vessel.—At the beginning of an experiment, both surfaces of the liquid under examination are under atmospheric pressure; by compression of the air in the reservoirs and drying tubes it is forced through the system of bulbs of the absorption apparatus. If, in all experiments, the same volume of liquid be taken, the amount displaced will be the same, and the internal pressure will be greater or less, according as the liquid employed is more or less dense. The internal pressure in some determinations varies slightly during their performance; the variation, however, never exceeds a millimeter or so of mercury. The use of a column of water to measure the internal pressure renders its determination very exact. The atmospheric pressure was found

to remain practically constant during an experiment, which seldom lasted more than an hour and a half. The error arising from the determination of the pressure to which the air in the interior of the apparatus is subjected, can accordingly be reckoned so slight as to be entirely negligible.

The mercury filled into the measuring vessel for the ballast, as well as the volume of water used to calibrate the same, can be measured to within a half cc., and as from 100 to 300 cc. of mercury and 1,000 to 3,000 cc. of water were taken, the error committed cannot be more than a thousandth of volume of air, and, in most cases, is probably less.

The air is, from the way it is forced from the measuring vessel, always measured when saturated with aqueous vapor. The drying tubes are always to be so filled with the drying reagents as to leave as little room as possible; I found, however, by special experiments, that the shape and size of the drying tubes exercise no appreciable influence upon the quantity of liquid carried off by the air; the only requisite seems to be that they dry the air thoroughly.

All the parts of the apparatus employed in measuring the volume of air being completely submerged in the water of the thermostat, there is no possibility of error arising from non-uniformity of temperature. The temperature of the water which expelled the air was, in most of my experiments, about 20° lower than that of the thermostat, but it entered the measuring vessel so slowly that it took on the temperature of the bath without disturbing, to any appreciable degree, the prevailing thermal conditions. That the water introduced took on rapidly the temperature of the bath was proven by the circumstance that, when, at the end of a determination, the flow of the water was stopped, and the level of the letter was flush with the guage-mark, if the measuring vessel, which in this condition might be said to be a rude but still quite delicate thermometer, was allowed to stand undisturbed for some time, no expansion or, at most, but very slight expansion of the water occurred.

Error from Change of Concentration of Mixture.—A source of error is to be found in a possible change of the concentration caused by one or the other of the components of the mixture

being carried off by the air in such quantity that the composition of the residual mixture is not the same as at the beginning of an experiment; I think, however, that the error introduced in this manner is so slight as to be practically negligible, and for the following reasons:

1. The shape of the absorption vessel is such as to form five chambers almost entirely independent of one another as far as their contents are concerned. The stream of air becomes saturated in passing through the first two or three bulbs, and passes through the last two without changing, to an appreciable degree, the composition of the mixture contained in them. That saturation is complete after the air has been passed through the first three bulbs, I assured myself by special experiments; that is, I filled only the three first bulbs, and found, on passing a certain volume of air through them, that the evaporated quantity of liquid was the same as when the same volume of air under similar conditions was passed with all the bulbs filled with the liquid.

2. As from forty to eighty grams of solution were taken in a determination, and as the quantity evaporated rarely exceeded two grams, it is evident that, even if, towards the last of the experiment, the concentration of the first bulb had altered somewhat, the composition of the mixture in the fifth bulb would remain practically unchanged.

3. Most of the mixtures examined were made up of liquids possessing not greatly different vapor-tensions, so that the vapors of both liquids passed off in about the same proportions.

Error in Analysis of Mixture of Vapors.—The mixture of vapors on escaping from the absorption vessel passes into the U tube, and thence through the lead tube into the analyzing tube. In order that no vapor may condense in the end of the U tube flared out for the reception of the cork through which passes the outlet tube of the bulb apparatus, the latter tube is ground into the horizontal branch which is somewhat constricted for that purpose; the cork is employed to give solidity and stiffness to the juncture. It is believed that by this means all the vapor passes into the horizontal branch of the U tube where it is directly exposed to the action of the entering current of air.

Necessarily, the outer branch of the U tube has to project a little out of the water of the bath in order that the lead tube may pass over the side of the thermostat; hence, as the upper part and the lead tube are generally at lower temperature than the water of the bath, some condensation of the vapors occurs; the condensed vapor runs down the tube to collect at the bottom. In order to vaporize this liquid and cause it to pass over the glowing lime, it is necessary to pass a current of air through the tubes to complete the determination. In this operation, two sources of error may be encountered: First, when the connection between the absorption vessel and the U tube is broken, some of the vapor with which the tubes are filled may diffuse out and be lost; and second, the vapor may be carried along too rapidly with the air to permit of its complete decomposition by the heated lime. There seems to be no simple means of avoiding slight loss of vapor; still, by careful manipulation and rapid operation, the loss may be rendered insensible.

My mode of operation was as follows: Holding between the thumb and first finger of my right hand the little stopper of the absorption vessel, and between the thumb and the first finger of my left hand the cork and tube to be fitted into the horizontal branch of the U tube, I withdrew the cork, and at once inserted in the U tube the cork and tube. The time that the ends of the pieces of apparatus were open was less than two seconds, so that the loss must have been minimal.

A circumstance which aids in the prevention of loss by diffusion is, that the heated lime tube causes a slight draft towards it when the U tube is open. It is certainly legitimate to conclude that the error from this source is exceedingly slight.

In regard to the second source of error the greatest precautions must be taken to prevent its assuming disturbing proportions. As soon as the connection between the absorption vessel and the U tube has been secured, the pinch-cock on the end of the rubber tubing (see page 633) is closed a little so that air is drawn in a slow stream through the tubes at first, and faster afterwards (see page 634). The amount of error due to this source is best determined by special experiments in which a weighed quantity of a pure halogen compound is introduced

into the absorption vessel, a certain volume of air passed through it, all the usual precautions in determining a vapor-tension being observed, and a comparison made between the loss by vaporization and the amount of the compound calculated from the quantity of halogen found in the lime; naturally the loss should, in case no error of experimentation has occurred, be equal to the quantity of liquid corresponding to the halogen found by analysis. Two experiments were carried out, one with carbon tetrachloride, and the other with chloroform. The difference between the weights and the liquids before and after the passing of the air was for chloroform 1.9014 grams, and for carbon tetrachloride 2.0178 grams; the results of analysis gave the amount of chloroform to be 1.9022 grams and that of carbon tetrachloride 2.0167 grams. As is seen, the differences between the two sets of results are not more than those due to the errors of analysis, and it seems that the error due to the analysis of the mixture of the vapors is very slight.

When an acid is in the mixture whose vapor-tension is being determined, the error attendant upon the determination of the amount vaporized cannot be more than that incurred in a titration, since there is no chance for the acid to escape, so quickly and directly is it brought in contact with the absorbing alkaline liquor. In a special experiment, the loss of acid from the absorption vessel was 0.2908 grams, while a titration of the solution of baryta gave as the amount of acid 0.2896 grams.

While the errors of the experimental method here described seem to be slight, there is an error that may have been committed in the assumption which lies at the basis of our calculations; when the volume of a vaporized liquid is large in comparison with the total gaseous volume, it is very probable that the vapor cannot be likened even approximately to an ideal gas. This point will be discussed in the following section.

6. COMPARISON OF THE VAPOR-TENSIONS OBTAINED BY THE METHOD HEREIN DESCRIBED AND THOSE OBTAINED BY OTHER METHODS.

Probably the best way to judge of the accuracy of the results

obtained in the determination of the vapor-tensions of liquids according to the method described in this paper is to compare them with the results obtained by other investigators working by other methods. Also a criterion of accuracy is to be found in the more or less close concordance of duplicate experiments. In the following table are given the necessary data of my experiments together with the results obtained by others. It was in some cases necessary to interpolate the results of others inasmuch as my results referred to a limited number of temperatures; the interpolations were made on a large scale, so as to avoid any slight inaccuracy. The original papers of Young and Regnault I am now unable to consult, and have to take their data as given in Landolt and Börnsteins "Physikalisch-Chemische Tabellen" or other reproductions.

TABLE II.[1]

Vapor Tensions of Pure Liquids.

Name of liquid.	Temperature.	Loss in grams.	Volume of loss in cc.	Volume of air in cc.	Internal pressure in mm. Hg	Barometer in mm. Hg.	Tension of vapor in mm. Hg.	Tension according to other observers.	
Benzene	34.8°	1.3805	443.	1876	5	760	145.4	147.2	(Y)
Monochlorbenzene	34.8°	0.2291	5.1	1883	10	757	20.3	20.0	(Y)
Monobrombenzene	34.8°	0.1289	2.0	1888	10	757	8.0	8.0	(Y)
Toluene	34.8°	0.2451	67.6	1014	11	754	46.8		
"	34.8°	0.4672	128.9	1949	11	754	46.7		
Metaxylene (not especially purified)	34.8°	0.1080	25.8	1201	17	757	4.17		
Metaxylene (not especially purified	34.8°	0.1085	25.9	1201	17	758	4.18		
Nitrobenzene	34.8°	0.0090	1.85	1210	23	757	1.16		
"	34.8°	0.0088	1.83	1207	21	757	1.15		
Carbon tetrachloride	34.8°	3.3803	5.55	1913	20	758	169.4	172.6	(R)
" "	27.8°	2.4031	3.96	1908	18	756	130.0	130.8	(R)
Chloroform	35.0°	3.0320	64.48	1033	25	755	290.1	301.1	(R)
Ethyl iodide	34.8°	4.2091	683.	1913	20	756	199.0	206.0	(R)
" "	27.8°	2.9760	483.	1918	22	756	152.2	154.7	(R)
Carbon bisulphide	20.0°	2.4541	777 4	1206	21	756	296.4	298.1	(R)
Methyl formate	20.0°	5.1090	195.8	1196	16	756	469.4		
Acetic acid	35.0°	0.2900	70.0	1960	20	760	26.3	26.5	(R&Y)

An inspection of the table shows a most excellent correspond-

[1] Bibliographical references to Table II: (Y)=Young; Chem. Soc. **55,** 486, *1889.* (R)=Regnault: Mèmoires de l'Academie, **26,** 239, *1862.* (R & Y) = Ramsay & Young, Chem. Soc., **49,** 790, *1886.*

ence between my determinations of vapor-tensions and those of others, when the liquid is but slightly volatile, as in the case of the halogen substitution products of benzene. But when, at the temperature taken for a determination, the elastic force of the vapor exceeds one hundred mm. of mercury, the correspondence becomes less close; and it is at once seen from the data that the greater the volatility of a liquid, the greater the discrepancy. Let us take carbon tetrachloride and ethyl iodide for examples, since determinations of their vapor-tensions were carried out at two different temperatures. For carbon tetrachloride the difference between Regnault's results and mine is three and two-tenths mm. of mercury at 34.8° and eight-tenths mm. of mercury at 27.8°; for ethyl iodide, the difference at 34.8° is seven and one-tenths mm. of mercury, and at 27.8° one and five-tenths mm. of mercury. Other examples point to the same result.

The cause of this want of concordance between my results and those made by other methods has been hinted at in the last paragraph of the discussion of the errors to which this method is subject. The assumption, made in the calculations, that the vaporous mixture may be treated as a mixture of ideal gases, cannot be maintained when the volume of the vaporized liquid forms more than a small fraction of the total volume of the gaseous mixture that leaves the absorption vessel. The vapor of ethyl iodide that was carried off by the air, occupied more than a fourth of the total volume, and the other volatile liquids also occupied relatively large volumes; the volumes of the vapors of the less volatile liquids, however, were but a small part of the volume of the air passed through the liquid. And, as has been shown, the less volatile liquids give results perfectly concordant with those obtained by others. Duplicate determinations of the vapor-tensions of some of the liquids, as toluene, nitrobenzene, etc., give almost identical results.

It would not be difficult to apply a correction taking into account the greater volatility of some of the liquids. This I have not, as yet, done, as in certain details I wish to alter the apparatus so as to obtain even more accurate results; thus the use of mercury as the liquid for expelling the air from the measuring

vessel would render the system of drying tubes unnecessary; also ground glass joints are undoubtedly preferable to rubber connections. Although it is my intention to study and modify the apparatus further, I do not want to seem to "reserve" this subject of investigation; on the contrary I would be most glad to see the apparatus tried and tested by others.

Although the results obtained by the employment of this method do not have in the case of the more volatile liquids the same degree of accuracy attainable by other methods, still they are suited to the requirements of an investigation of the vapor-tensions of mixtures of liquids, since both liquids, if their vapor-tensions be not too different, are affected alike by any weaknesses in the method, and the phenomenon observed permits of the drawing of theoretic conclusions. Yet I have been careful in the discussion of results to limit myself as much as possible to such as were of the same accuracy as results obtained by others; thus, my method can be counted upon to give results accurate to less than one mm. of mercury when the vapor-tension does not exceed 100 mm. of mercury, and to less than two mm. of mercury when the vapor-tension is less than 150 mm. of mercury; as can at once be seen by a comparison of the data due to Young (*loc. cit.*) and Regnault (*loc. cit.*) in the greater number of cases a closer correspondence than to within two mm. cannot be found. However, the conclusions which I draw from my experiments would still hold if the error in the determination were several times greater than that admitted above, inasmuch as it affects each liquid in the same way, so that, while it may affect the absolute accuracy, its relative effect is but slight.

7. CHOICE AND PURIFICATION OF LIQUIDS.

As stated previously, the liquids employed in the course of this investigation were those recognized to be strictly normal; and of those only such were chosen as can be gotten in a state of great purity. The only associated liquid taken was acetic acid, whose degree of association as well as whose physical properties are to a certain extent known.

An associated liquid was investigated for the purpose of apply-

ing the regularities and "normalities" discovered in mixture of normal liquids to mixtures of a normal liquid with an associated liquid. Great pains were taken to purify the liquids in the highest possible degree, it being the testimony of all those who have occupied themselves with experimental work on the vapor-tensions of liquids that even very slight impurities have a remarkably disturbing effect upon the accuracy of results; this is especially the case in results obtained by the static method; in the method employed by me, the influence of a slight amount of impurity is not so marked; still, for all that, it has been thought best to employ such material as had been most thoroughly purified.

In order that the readers of this paper may judge for themselves the degree of purity of the liquids examined, a somewhat detailed account of the method of purification of each liquid is given together with a statement of certain characteristic physical properties of each. All of the liquids, it may be stated beforehand were bought as chemically pure from the dealers (Poulenc Frères, Paris, and Billault, Paris), and at least one pound—generally two or three pounds—subjected to the purifying operations.

Benzene.—Nearly three pounds of benzene—labelled chemically pure and free from thiophene—were treated a half dozen times with sulphuric acid to remove last traces of the sulphur compound. The liquid was then repeatedly fractionally crystallized until about a pound was obtained melting at 5.3°. This purified product when partially solidified showed, no matter what the proportion of liquid and solid was, the same melting point. The whole was then distilled over a few pieces of sodium, no variation from the boiling point 80.1° under a pressure of 756 mm. of mercury being observed. Its specific gravity at 25° referred to water at the same temperature was found to be 0.876611.

Toluene.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at 109.8° to 110.1°, an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling constantly at 110.1° under a pres-

sure of 758 mm. of mercury. Its density at 25° referred to water at 25.0° was ascertained to be 0.86288.

Monochlorbenzene.—A couple of pounds of monochlorbenzene were repeatedly distilled in fractions until a constant boiling product resulted. About three-quarters of a pound were obtained, boiling at 131.8° to 131.9° under a pressure of 757 mm. of mercury, and having a density at 25.0° (referred to water at same temperature) of 1.10362.

Monobrombenzene.—Nearly a pound of brombenzene was fractionally distilled until a distillate was obtained boiling between narrow limits. About 150 grams of the product, boiling at 154.3° to 154.5° under a pressure of 761 mm. of mercury were obtained. The density at 25° referred to water at 25.0° was 1.49852.

Nitrobenzene.—The commercial article was repeatedly crystallized until an almost colorless liquid was obtained, which when solidified, showed the same temperature during the remelting. It possessed a melting point of 3.6°, and its density was 1.20201, $\left(\frac{25^\circ}{25^\circ}\right)$.

Chloroform.—About two pounds of "chloroform anesthétique" of commerce were washed a dozen times with water, dried thoroughly by means of fused calcium chloride, and distilled. The larger distillate boiled at 60.8° to 61.0° under a pressure of 751 mm. of mercury, and finally nearly a pound was obtained boiling at 60.9° under a pressure of 755 mm. of mercury.

Carbon Tetrachloride.—Two pounds were washed with water, and thoroughly dried by means of concentrated sulphuric acid. The product was then rectified, and nearly a pound boiling throughout the operation at 76.6° under a pressure of 756 mm. of mercury taken for the preparation of the mixtures. The specific gravity of this product at 25.0° referred to water at the same temperature was 1.58828.

Acetic Acid.—Two pounds of glacial acetic acid were repeatedly fractionally crystallized until a portion melting at 16.7° was obtained. The bottle containing it as well as the mixtures made

from it were kept under an air-tight bell-jar by the side of very strong sulphuric acid.

8. PREPARATION OF THE MIXTURES.

The mixtures were prepared by weighing out to a milligram on a balance turning with a tenth milligram the liquids in a flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from forty to one hundred grams of the mixture were weighed out, the composition of the liquid was thus known to a ten-thousandth at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and kept in a dry, cool, dark closet. As, almost invariably, the necessary vapor-tensions of a liquid were made immediately after its preparation, no change of concentration occurred even with the most volatile liquids employed.

In the case of some of the mixtures of benzene and carbon tetrachloride, the residues of the investigated mixtures were united, and the amount of chlorine in the resulting mixture determined according to Carius' method.

The mixtures of benzene or toluene with acetic acid had their concentration controlled by an analysis. Five to ten cc. of the mixture were carefully weighed out in a glass-stoppered flask, water was added, which took practically all the acetic acid from the benzene, and then standardized baryta water run in to point of neutralization. In no case did the analysis give results sensibly different from those calculated from the direct weighings.

9. EXPERIMENTAL RESULTS WITH MIXTURES OF NORMAL LIQUIDS.

In the following tables (III to X) are given those data of the experiments necessary for the calculation of the vapor-tensions. The superscriptions over each column of data render any preliminary mention here unnecessary. In some cases, the data have been represented graphically. (Figs. II. to IV.)

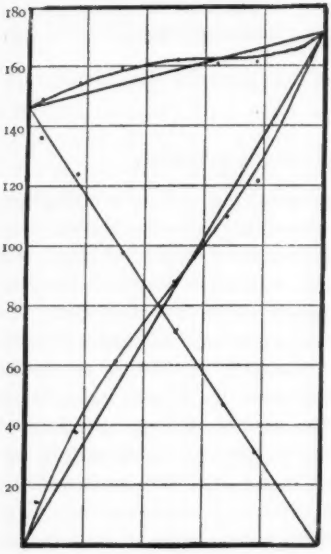

FIG. 2.

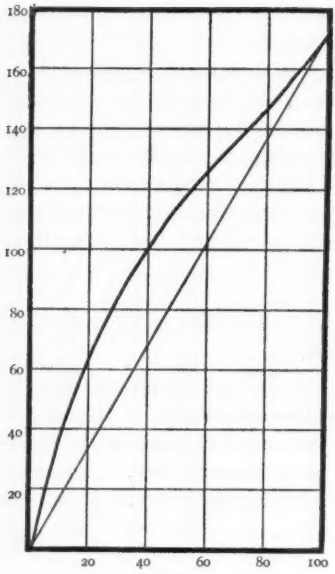

FIG. 4.

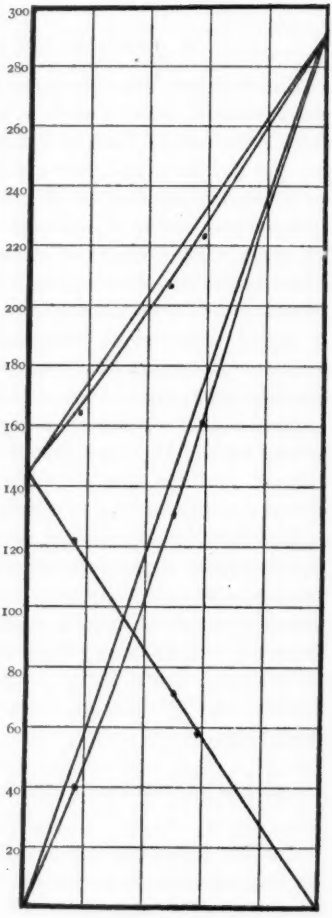

FIG. 3.

EXPLANATION OF FIGURES.

Fig. 2.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of CCl_4 in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 3.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of $CHCl_3$ in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 4.—Vapor-tensions of mixtures of nitrobenzene and carbon tetrachloride.

Abscissas= molecules of CCl_4 in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

TABLE III.

Vapor-Tensions of Mixtures of Benzene and Monochlorbenzene at 34.8°.
Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.
Vapor-Tension of Chlorbenzene at 34.8° is 20.3 mm. of Mercury.

Molecules C_6H_5Cl in 100 molecules of liquid mixture.	Molecules C_6H_5Cl in 100 molecules of gaseous mixture.	Grams C_6H_5Cl in vapor.	Grams C_6H_6 in vapor.	Tension of C_6H_5Cl in mm.	Tension of C_6H_6 in mm.	Volume of air in mm.	Barometer in mm.	Internal pressure in mm.
15.18	1.33	0.0454	2.3075	1.7	124.6	3782	763	11
29.08	6.11	0.0857	0.9143	6.6	101.3	1900	757	17
65.06	19.37	0.1800	0.5202	12.3	51.3	2032	758	18
79.21	35.15	0.3572	0.4750	19.1	27.9	3787	756	12

TABLE IV.

Vapor-Tensions of Mixtures of Toluene and Monochlorbenzene at 34.8°.
Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.
Vapor-Tension of Chlorbenzene at 34.8° is 20.3 mm. of Mercury.

Molecules C_6H_5Cl in 100 molecules of liquid mixture.	Molecules C_6H_5Cl in 100 molecules of gaseous mixture.	Grams C_6H_5Cl in vapor.	Grams C_7H_8 in vapor.	Tension of C_6H_5Cl in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
18.96	9.84	0.0510	0.3821	4.3	38.2	1963	757	17
41.82	22.66	0.0985	0.2754	8.1	27.6	1973	760	21
76.71	67.79	0.2089	0.0821	17.5	8.2	1965	757	18

TABLE V.

Vapor-Tensions of Mixtures of Benzene and Monobrombenzene at 34.8°.
Vapor-Tension of Benzene as 34.8° is 145.4 mm. of Mercury.
Vapor-Tension of Brombenzene at 34.8° is 8.0 mm. of Mercury.

Molecules C_6H_5Br in 100 molecules of liquid mixture.	Molecules C_6H_5Br in 100 molecules of gaseous mixture.	Grams C_6H_5Br in vapor.	Grams C_6H_6 in vapor.	Tension of C_6H_5Br in mm.	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
30.33	24.30	0.0395	0.4975	2.6	103.1	1018	757	13

TABLE VI.

Vapor-Tensions of Mixtures of Benzene and Chloroform at 34.8°.
Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.
Vapor-Tension of Chloroform at 34.8° is 289.2 mm. of Mercury.

Molecules $CHCl_3$ in 100 molecules of liquid mixture.	Molecules $CHCl_3$ in 100 molecules of gaseous mixture.	Grams $CHCl_3$ in vapor.	Grams C_6H_6 in vapor.	Tension of $CHCl_3$ in mm.	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
16.97	24.30	0.3243	0.6607	39.6	123.5	1032	755	25
50.53	63.74	1.1513	0.4187	130.7	74.3	1030	756	25
59.47	73.25	1.4770	0.3531	162.2	59.2	1030	749	25

[TO BE CONTINUED.]

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 2.]

THE ELECTROLYTIC DETERMINATION OF RUTHENIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.

Received April 22, 1895.

FROM time to time efforts have been made in this laboratory to gather information upon the deportment of the metals of the platinum group toward the electric current. Palladium, platinum, and rhodium have been determined quantitatively, and also separated electrolytically from other metals of the group, *e. g.*, palladium from iridium. The purpose of this communication is to present data relating to the electrolysis of ruthenium salt solutions. The literature of electrolysis does not contain any information upon this point.

The salt upon which the experiments were made was the double chloride of potassium and ruthenium. It was prepared by fusing the finely divided metal with potassium nitrate and hydroxide. This fusion was made in a silver crucible. The aqueous extract was acidified with hydrochloric acid, and the solution was then evaporated to crystallization. Much potassium chloride separated at first, but finally the double salt appeared in minute red-colored needles.

The platinum dish in which the electrolytic decomposition was carried out was coated upon its inner surface with a layer of copper. In the first trials the solution of the double salt was mixed with three grams of sodium acetate, and acted upon by a current of N. $D._{100}$ = 0.01–0.05 ampere. The quantity of the ruthenium salt not being very abundant it was necessary to conduct the determinations with rather small amounts of material.

Thus, fifty cc. of the double chloride solution contained 0.0593 gram of ruthenium metal. The results of four trials were:

1 ..... 0.0119 gram of ruthenium in five cc. of solution, equal to 0.0595 gram in fifty cc.
2 ..... 0.0589 gram in fifty cc. of solution.
3 ..... 0.0593 " " " "
4 ..... 0.0590 " " " "

The metal deposit in each instance was dull black in color. A tendency to sponginess was also observed.

As other metals of the platinum group had been precipitated successfully from a phosphate solution (*Am. Chem. J.*, **13**, 206) ruthenium was tried under similar conditions.

In the experiments that follow, fifty cc. of the salt solution contained 0.0407 gram of metal. Fifteen cc. of disodium phosphate (1.0358 sp. gr.) and one cc. of phosphoric acid were added to this solution. The current was of the same strength as that used in the first series of experiments. The metallic deposits weighed:

1..... 0.0402 gram.
2..... 0.0407 "
3..... 0.0413 "

The ruthenium in each instance was bright and steel-like in appearance. It was also very adherent. There was not the slightest indication of sponginess. In the two series just given the deposit of metal was washed first with warm water, and subsequently with absolute alcohol. The period of precipitation continued through the night, although six hours were found to suffice for the complete deposition of the ruthenium.

In a third series of two trials, fifty cc. of the salt solution contained 0.0100 gram of ruthenium. The phosphate, phosphoric acid, and the current were the same as in the series immediately preceding. Results:

1 ..... 0.0101 gram ruthenium.
2 ..... 0.0100 " "

The deposits, as before, were bright and apparently crystalline.

Mention has already been made that palladium and platinum could be separated electrolytically from iridium (*Am. Chem. J.*, **16**, 435) when present together with the latter in a phosphate solution. This was, however, not found possible with rhodium, although this metal was successfully deposited from a similar

solution. As ruthenium, from the results just given, allies itself with palladium, platinum, and rhodium, so far as its deposition from a phosphate solution was concerned, it seemed of interest to ascertain whether a separation of it from iridium could be effected.

Separation of Ruthenium from Iridium.—Here again a solution of ruthenium was used in fifty cc. of which there was 0.0100 gram of ruthenium. To this were added ten cc. of an iridium solution (equal to one-tenth gram of iridium), ten cc. of disodium phosphate, 1.0358 sp. gr., and three cc. of phosphoric acid. The current was N. $D._{100}$ = 0.01 ampere. It acted through the night. The deposit of ruthenium in each of the three experiments was bright, metallic, and perfectly adherent. It was washed and dried as in the determinations described in the preceding lines. Results:

1..... 0.0104 gram of ruthenium.
2..... 0.0096 " " "
3..... 0.0100 " " "

Additional experiments on the separation of the two metals were made with similar results.

It would be of interest and value to study the conduct of ruthenium in alkaline solutions. Wöhler[1] observed that the metal could be quickly brought into solution when the current acted upon it in the presence of an alkali. It is altogether probable that, under such conditions, its separation from the other metals of the group could be quite readily brought about, but lack of material will, at least for the present, prevent any such investigation.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 3.]

THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON THE DIOXIDES OF ZIRCONIUM AND THORIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.

Received May 31, 1895.

SOME years ago Weber (*Jahr. 1859*, 77) studied the action of phosphorus pentachloride upon inorganic oxides, such as those of silicon, titanium, and tin, and demonstrated that the

[1] *Ann. Chem.* (*Liebig*), 146, 375.

products of the reaction were the corresponding metallic chlorides, together with phosphorus oxychloride. Tüttschew (*Jahr. 1867*, 205), working upon titanium dioxide with a modified method, obtained a double chloride corresponding to the formula $TiCl_4.PCl_5$.

It seemed to us of some interest to extend the study to the oxides of zirconium and thorium, thus completing the reaction with the more metallic bodies of Group IV of the periodic system. The procedure adopted by us consisted in introducing ignited and pure zirconium dioxide with its equivalent of phosphorus pentachloride into hard glass tubes, which were sealed after the air had been exhausted from them. The reaction appeared not to occur at 150° C., but after heating to 190° C., for a period of eight hours, a complete change was observed. A crystalline mass was noticeable and drops of phosphorus oxychloride were scattered through the tubes. These were opened at both ends and quickly connected with a chlorine generator, and distillation carried out by careful heating in an air-bath. Phosphorus oxychloride and some pentachloride were expelled. At 190° C., crystals made their appearance in the cooler part of the tube, projecting beyond the air-bath. These were transparent and almost half an inch in length. That portion of the tube in which they had collected was severed, tightly closed, and weighed. It was then introduced into water. A hissing sound was quite distinct. Zirconium hydrate soon separated. After standing a while this was dissolved in dilute nitric acid, and reprecipitated with ammonia. Later it was found that to let the weighed chloride slowly absorb moisture from the air and then bring it into water insured better results. The percentage of zirconium found equaled 37.52 per cent., while the chlorine was 61.62 per cent. The theoretical requirements for the tetrachloride are 38.79 per cent. of zirconium and 61.21 per cent. of chlorine. Our zirconium result is low, yet the figures from three or four analyses concord so closely that there can be no question as to the correct nature of our product. A compound of zirconium chloride with either phosphorus pentachloride or oxychloride would require decidedly less zirconium and more chlorine. Hence, we can safely conclude that with our conditions

of experiment phosphorus pentachloride changes zirconium dioxide to the corresponding chloride. Thorium dioxide was subjected to a similar treatment. The temperature, however, at which the reaction seemed to proceed almost to completion was about 240° C. Exactly the same course was pursued in subsequently eliminating the excessive phosphorus compounds. The product analyzed showed the presence of a little phosphorus, not enough to establish the existence of a double chloride, therefore its quantity was deducted from the quantity of material used in the analysis. The thorium found equaled 62.23 per cent. and the chlorine 38.37 per cent., while the theoretical requirements for thorium tetrachloride are 62.23 per cent. thorium and 37.77 per cent. chlorine.

Our experiments supplement the investigations of Weber and justify the general inference that the dioxides of all the metallic members of Group IV are changed to tetrachlorides when heated under pressure with phosphorus pentachloride.

UNIVERSITY OF PENNSYLVANIA.

NEW BOOKS.

A TEXT-BOOK OF CHEMISTRY INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS. BY SAMUEL P. SADTLER AND HENRY TRIMBLE. Octavo, pp 950. Philadelphia: J. B. Lippincott & Co., 1895.

The title on the cover is "Pharmaceutical and Medical Chemistry," from which it is to be regretted that the authors did not omit the word "Medical," as its use compels a remonstrance against the view which they apparently entertain, that the needs of the medical student in the department of chemistry do not extend beyond the study of the properties of drugs and the methods of chemical manufacture. Physiological, hygienic and toxicological chemistry are almost utterly ignored. A mere outline of the chemistry of urea is compressed into less than a page, while more than two pages are devoted to alizarin. Serum albumen is dismissed in four lines, without a word about the testing of urine for albumen. The discussion of the degrees of purity of natural waters is barely hinted at in a few lines, without any reference to the methods of examination of water, even

in the part devoted to analytical chemistry. The space allowed to the toxicological chemistry of arsenic is only three-quarters of a page, while the metallurgy of iron occupies four and three-quarter pages. To designate such a work as a "Medical Chemistry" is, to put it mildly, a misnomer.

Viewed, however, as a text-book for the use of the student of technical chemistry or the manufacturing pharmacist, the work is, in most respects, well arranged and, in the main, up to the times, although in some points somewhat too conservative. Such terms as acid potassium sulphate, copper sulphate, calcium phosphate, sodium sulphate, acid calcium phosphate, either have the ring of antiquity or lack precision. The orthography endorsed by the A. A. A. Sc. has not been adopted.

The work is divided into five parts. Part I contains, in 90 pp., a brief outline of elementary physics, which is rather popular and general than chemical or medical. The laws of Dulong and Petit and of Raoult are not mentioned, absorption spectra are merely referred to, and the description of the errors of refraction of the eye is not only fragmentary but misleading.

Parts II and III (182 and 243 pp.) treat of mineral chemistry. The elements are classified into "non-metals" and "metals," a division which widely separates nitrogen and phosphorus from their close relations to arsenic and antimony. Methane, ethane, acetylene, and the oxides and sulphides of carbon are treated of as universal substances in Part II. Descriptions of the methods of preparation of the elements and their compounds, and statistics of industrial production are detailed and illustrated by numerous familiar cuts of furnaces and other forms of manufacturing plants. Pharmaceutical references are in accordance with the last revision of the U. S. Ph.

Part IV (280 pp.), devoted to organic chemistry, is admirably written. The arrangement is logical and scientific, and the matter is abreast of the advances in this most important division of chemistry, and as full as is desirable or possible in a work of this size. But in this division, also, it is to be regretted that the space occupied by pictures and details of manufacturing apparatus and processes was not devoted to medical chemistry.

Part V (94 pp.) contains the analytical portion. The reac-

tions of bases and acids are given with conveniently arranged tabular schemes of qualitative analysis. There are also a few examples of quantitative methods, and descriptions of the more important processes of drug assay. The work concludes with an appendix containing useful tables. R. A. WITTHAUS.

JOHN DALTON AND THE RISE OF MODERN CHEMISTRY. By SIR HENRY E. ROSCOE. New York and London. Macmillan & Co., 66 Fifth Avenue, New York City. Price, $1.25. pp. 216; 12 mo. Portrait and facsimile. The Century Science Series.

This is an unusually satisfactory book; it is a pleasure to read the biography of one eminent man written by another distinguished in the same branch of knowledge, who appreciates and sympathizes with his subject and his subject's labors.

Materials for a history of John Dalton and his contributions to chemistry were not lacking. W. C. Henry's "Memoirs" (1854), R. A. Smith's "Memoir and History of the Atomic Theory" (1856), Charles Clay's "Reminiscences" (1884), and Lonsdale's "Worthies of Cumberland" (1874), supply the necessary details of the uneventful, quiet life of the Manchester schoolmaster, and accounts of his momentous researches in chemical philosophy. Besides these sources of information, Sir Henry could refer to his own lecture delivered in the Town Hall, Manchester, in 1874. In this volume we find a summary of Dalton's parentage, school days, and teachers, his experience as a school teacher when only twelve years of age, his first attempts at scientific investigation (meteorological), his connection with the Manchester College, and his pains-taking researches on the relative weights of ultimate particles. The text is pleasantly anecdotal, clearly describing Dalton's personality. The volume is illustrated with a portrait of Dalton, facsimiles of letter and leaflet containing the atomic symbols. One remark of Sir Henry's greatly surprises us; speaking of decimal fractions he says they are "a snare and a stumbling-block even to some great men of the present day." Can it be that calculations in £, *s*, and *d*. are so deeply impressed on the British mind that they prevent comprehension of decimals familiar to every American schoolboy? The book contains an excellent index.

H. CARRINGTON BOLTON.

DR. GIDEON E. MOORE.

Received May 31, 1895.

THE death of Dr. Moore happened on Saturday, April 13, 1895. On the following day the death of Prof. James D. Dana was announced. The occurrence so closely together of these sad events was a striking one, for it was under the guidance of Prof. Dana that Dr. Moore entered upon a field of study which he cultivated with so much ardor that his reputation for deep scientific work was increased; and we may well believe that, had not the accidents of fate and fortune turned Dr. Moore's steps from academic halls he, also, would have left the impress of his good and strong personality upon the mind and life of many a youthful student of science.

Gideon Emmet Moore, son of George H. and E. L. Moore, was born in New York City, August 21, 1842. His maternal grandfather, after whom he was named, was Dr. Gideon Humphrey, one of the leading physicians of Philadelphia in the beginning of this century, who distinguished himself as a surgeon in the war of 1812, and took part with remarkable adventures in the filibustering expeditions of the period. His father, whose family belonged in Maine, early went to California, in fact was one of the first settlers of San Francisco, as he was there eleven years before the Argonauts of '49. He embarked in the business of shipping and warehousing, and his firm was the foremost one of the time.

Young Gideon Moore's early days were spent, some in New York and some in Burlington, N. J., and, before entering Yale College, at Dr. Bartlett's Academy in Poughkeepsie. In his boyhood he was passionately fond of music and an accomplished performer on the violin. His class at Yale was '61. Prof. S. W. Johnson has kindly sent me the following tribute to his pupil:

"Our friend, Gideon E. Moore, entered the Yale Scientific School in the Autumn of 1859, graduated as Bachelor of Philosophy in the Summer of 1861, and remained as a postgraduate student until the Spring of 1862.

"During the first year of his attendance I knew him slightly, but from September 1860 until he finished his studies I had immediate charge of the Laboratory of Analytical Chemistry and was constantly familiar with his progress in chemical study. I was from the outset attracted by the gentle and courteous manners of the somewhat delicate appearing youth whose invariable cheerfulness, promptitude, and steady attention to work, no less than the ease with which he performed and exceeded the tasks assigned him, made the duty of his teacher a pleasure and a privilege.

"Having gone through an extended course of inorganic analysis with unusual rapidity and success he was well prepared to take up organic chemistry, and the proposal was made to him (I think in Sept. 1861) to undertake an investigation of Bayberry Wax.

"This research was foreseen to require a long time and to involve much tedious labor, but he entered upon it without hesitation, pursued it steadily for four months, and evidently enjoyed it heartily to the end.

"The results are embodied in his paper—'On the Chemical Constitution of the Wax of the Myrica Cerifera'—which appeared in the American Journal of Science, May, 1862. This short paper, of seven pages, presents a concise history of the chemical work previously done on the bayberry wax and established its nature as a mixture of about one-fifth part of tripalmitin and four-fifths nearly of palmitic acid with a little laurin or lauric acid. It illustrates the thoroughness which characterized his work and which made him so immediately successful when, soon after completing his studies at New Haven he engaged in the practice of analytical chemistry at San Francisco, and later when he became assayer to the Gould and Currie mine at Virginia City.

"As I write these lines there stands near by a series of twenty little bottles containing specimens of the fruit, foliage and wax of the bayberry and the preparations obtained during the research in question illustrating the method followed and showing the results arrived at. This instructive collection has done duty regularly for thirty-two years in my lectures and recalls vividly to my remembrance the busy days when our friend was diligently disciplining to extraordinary skill the hand that but a few hours ago suddenly forgot its cunning."

Yours very truly,

S. W. JOHNSON.

Dr. Moore's life in the West was hard enough to daunt the most courageous but he viewed it as a necessary step in his

progress. The rough life of the mining camp and the hardships of that primitive era had no terrors for him. The very task itself of keeping a foothold in such a community only spurred him to accomplish what he had set out to perform, just as in his college and professional career to suggest that a matter was difficult, was sufficient to fire his ambition to attack it and his confidence that he would overcome it.

After four years spent in this field, enjoying in the highest degree the confidence of the owners of the millions which passed through his hands, he resigned to embrace with enthusiasm the opportunity to secure what he had so long coveted—a thorough course at the German universities.

In 1867 he sailed for Europe and studied one year at Wiesbaden under Fresenius. He next went to Heidelberg and under Bunsen, Kirchoff, Helmholtz, Blum, Vonderden, and Kopp he passed some of the happiest days of his life and was graduated *summa cum laude*. At Leipzig he studied under Kolbe one semester, and at Berlin in the laboratory of Wichelhaus.

In September, 1871, he married in Buda Pest, Marie Louise Von Hildebrandt, the daughter of Field Marshal Von Hildebrandt, of the Austrian army, and in the following month returned to America.

In 1872 he became chemist to the Passaic Zinc Co., and continued in that capacity to the close of his life. The remainder of his time was devoted to study and private practice, a field in which he rose to eminence and left a record marked with many triumphs.

Depth, care, thoroughness, and method characterized his work. His intellectual endowment was generous, his mental faculties keen, his memory good, his power of concentration wonderful. He possessed a logical and well-balanced mind not easily led to hasty conclusions. The virtue of strict, unwavering conscientiousness and fidelity to truth was a shining one in Dr. Moore, and his professional honor was not a mantle to be put on and off or to be distinguished from his personal honor. All his early training as well as the promptings of his heart fortified him in the practice of making diligent search for the truth, and having found it, of fighting bravely for his convictions.

He at one time wrote much and all of it was valuable; in the early days making many contributions to mineral chemistry; Brushite, Cryptocallite and Hetaerolite being additions made by him to the list of new species. Of late years his most laborious work, that on the "Chemistry of American Tobaccos," was written for the Tenth Census. He was editor of Vol. II of this JOURNAL, and in Vol. I appeared his report on the Progress of Analytical Chemistry for 1879—a model for all of its kind. He had taken out many patents in metallurgical and fuel-gas processes.

Subjoined is a list of his published papers:

1862. On the Chemical Constitution of the Wax of the Myrica Cerifera. American Journal of Science, [2], 33, 313.

1865. On Brushite, a new mineral species. American Journal of Science, [2], 39, 43.

1866. Analysis of the Water of Borax Lake, Cal. American Journal of Science, [2], 41, 255.

1870. On the occurrence of Amorphous Mercuric Sulphide (Metacinnabarite) in Nature. J. prakt. Chem., [2], 2, 319. American Journal of Science [3] 3, 36.

1871. On the Electrolysis of the Substituted Derivatives of Acetic Acid. Ber. d. chem. Ges., 4.

1875. On Chalcophanite, a new mineral species. American Chemist, July, 1875.

1877. On Hetaerolite, a new mineral species. American Journal of Science, [3] 14, 423.

1878. Report on the Strong System of Water-gas Manufacture. Engineering and Mining Journal, January, 1878.

1879. Report on the Progress of Analytical Chemistry, from April to September. J. Am. Chem. Soc., 1.

1883. Report on the Chemistry of American Tobaccos. Special Report of the United States Census, On the Culture and Curing of Tobacco. Chap. 22.

1885. Report on the Granger Water Gas. A. O. Granger & Co., Philadelphia.

1885. Kallait, pseudomorph of Apatite from California. In collaboration with V. von Zepharovich. Ztschr. für Krystallographie, Leipzig.

Dr. Moore's manners were gentle and courteous in the extreme. He used to tell with much appreciation how, when he was working in Bunsen's laboratory, he would always have to keep his eyes averted from Bunsen, who would immediately spring to his side were he to show the slightest sign of effort over the task or

the need of anything. And listening to him telling this you could not help thinking how marked was the same kindliness in himself. How grateful is association with such men. What a privilege to have daily converse with one whose soul delights in those little amenities which the throng overlook. What a pleasure in the cheery face. What a lesson we learn from the lips that may be quivering with pain, but open only to express solicitude for our welfare and to smile that they may hide their own story.

An acquisition that was of great value to our friend was his retentive memory. Everything that he had once mastered, whether in science or in other branches of knowledge, could be recalled to mind at will and with an accuracy and fidelity to detail that made us marvel. I remember on one occasion when in a leisure hour we were discussing the poets, and Coleridge became the subject of our remarks, he recited without hesitation the lines in Kubla Khan:

> "But oh that deep romantic chasm which slanted
> Down the green hill atwart a cedarn cover!
> A savage place! as holy and enchanted
> As e'er beneath a waning moon was haunted
> By woman wailing for her demon lover!"

I said "You have been reading Coleridge lately?" "No," said he, "I don't suppose that I have read these lines in over twenty years, but I remembered them for I always admired their sonorousness and picturesque effect."

He was a poet himself of no mean order. His nature was essentially grave, retired and full of self-repression, yet it had that expanding joyousness which goes in search of the delights that we may draw from elevated themes and roseate imagery. He had translated much from Gœthe, and more recently Hamerling, in lines which show alike his skill as a linguist and his art as a poet.

His end came suddenly, for he was stricken without warning, and he laid down his work to go and face the terrors of pneumonia. He did face them, and unflinchingly, and he calmly awaited the end, that he saw must come, with the fortitude of the Christian faith that he was glad to acknowledge.

CHAS. F. MCKENNA.

I spent last Saturday with Prof. T. E. Thorpe in his steam launch on the Thames at Kingston with a party of friends. He asked me then about Dr. Moore's death and spoke of him very warmly. They were students together in Germany and the friendship then formed was cemented by meetings during Thorpe's visit to America afterwards. He detailed at length, incidents of Dr. Moore's student and family life illustrating his lovable character.

Proof of Mr. McKenna's notice came to me in London, and I have ventured to add this note to show that his and Professor Johnson's words find an echo abroad. EDWARD HART.

London, June 22, 1895.

LOTHAR VON MEYER.

BY the sudden death of Lothar von Meyer, which occurred at Tübingen, on April 11th, chemical science has lost one of its foremost exponents.

It was vacation time in Tübingen, and Professor Meyer had returned from a walk and was engaged in his favorite outdoor pastime of trimming vines in his garden when he suddenly began to feel unwell and hastened to his study. He called for help and his wife and son went to his aid. Reaching a sofa with their support he remarked, "I have received a stroke," and then was able to say no more. This was at about 5 in the afternoon, and at 11 he died, without further struggle, his face retaining the calm and noble expression not to be forgotten by his many friends.

Julius Lothar Meyer was born August 19th, 1830, at Varel in the Grand Duchy of Oldenburg, the son of a well-known physician, Dr. August Meyer. He completed his gymnasium course in Oldenburg and began the study of medicine in Zürich in the Spring of 1851. There he spent four semesters, followed by two semesters at Würzburg, where he received the degree of Doctor of Medicine, in the Spring of 1854, for a thesis on the question of the condition of gaseous combinations in the blood. In the investigation of this problem Meyer's attention was attracted to the recent work of Bunsen on gas measurements, and accordingly we find him next in Heidelberg, where he re-

mained five semesters, at a time and in a company since famous in the history of chemistry. He took up again the question of the gases held by the blood, and in a long investigation, published in 1857, he showed for the first time the real nature of the oxygen absorption. Magnus had shown at an earlier date that the oxygen absorbed by blood did not follow the Dalton-Henry law, but he attempted no explanation for this fact. It remained for Meyer to determine the quantity of oxygen, carbon dioxide, and nitrogen absorbed under different conditions, and to show that the absorption of the first must depend on chemical combination. This investigation attracted immediate attention.

Meyer's tastes now led him away from medicine and in the direction of pure chemistry, and especially toward physical chemistry. Leaving Bunsen, he went to the old university of Königsberg, attracted by the courses of lectures given by Franz Neumann on the subject of mathematical physics. He remained with Neumann three semesters. In the Spring of 1858 Meyer went to Breslau, where he was given the degree of Doctor of Philosophy for a dissertation on the absorption of carbon monoxide by the blood. In this dissertation it was shown, for the first time, that CO displaces O, volume for volume. The author soon afterwards became a *Privatdocent* for physics and chemistry, and, in 1859, was given the position of Director of the Chemical Laboratory of the Physiological Institute. Here he remained until 1866. In this interval he published a number of valuable papers, and the first edition of his famous work, "Die modernen Theorien der Chemie."

In 1866 he was called to the Forestry Academy of Eberswalde, in 1868 to the Polytechnicum of Karlsruhe, and in 1876 to the University of Tübingen, where he had just completed his nineteenth year of labor at the time of his death.

Lothar Meyer was the author of numerous valuable scientific papers, most of which appeared in *Liebig's Annalen* and in the *Berichte*. They handle mainly questions from the field of physical chemistry. In some of his earlier papers Meyer began the study of the relations existing between the atomic weights and physical and chemical properties of the elements. Their relations were soon formulated in his Periodic System of the Elements.

That Mendelejeff arrived independently at almost the same conclusions does not, in any measure, detract from the originality or value of Meyer's work. It is this work which has made his name best known among scientific men, but without it his purely experimental investigations would be sufficient to give him a high position among the great chemists of the time.

In recognition of his services to science, Meyer received the Davy medal of the Royal Society in 1882, was made a Foreign Honorary Member of the London Chemical Society, in 1883, Corresponding Member of the Prussian Academy of Sciences, in 1888, and in 1891 a Corresponding Member of the Russian Academy. In 1892 he was given a title of nobility by decree of the Würtemberg crown.

He was the author of the following works: "Die modernen Theorien der Chemie," first edition 1864, fifth edition 1884, a sixth edition the author had in preparation; "Die Atomgewichte der Elemente" (with Karl Seubert), 1883; "Grundzüge der theoretischen Chemie," first edition 1890, second edition 1893. The first and last of these books are well known in English translations.

It is not necessary, in this place, to speak of the high scientific value of Meyer's work, as that is a subject on which the literature itself speaks most plainly. He possessed great manual dexterity, and in glass-blowing and the construction of apparatus he had unusual skill. His style, as a lecturer, was simple and exceedingly clear, and in his everyday intercourse with students he displayed a kindliness of disposition and patience in explanation not often found with men whose time is as closely occupied as was his. Few investigators are willing to give from their private work the time which he freely gave to interested students.

Among his colleagues Meyer was cordially respected and beloved. Last summer he was appointed Rector of the University for the present year, and by other distinctions, as well, his popularity was shown. All who knew him mourn his loss as a man; chemists alone are able to recognize the loss to science.

J. H. LONG.